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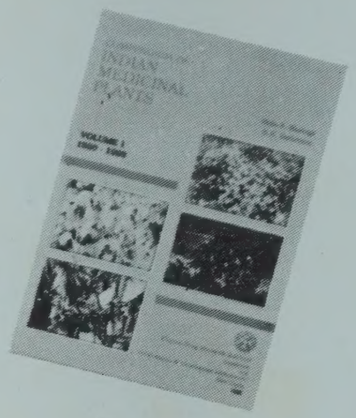
Compendium of Indian Medicinal Plants



4 Vols.

by R P Rastogi and B N Mehrotra

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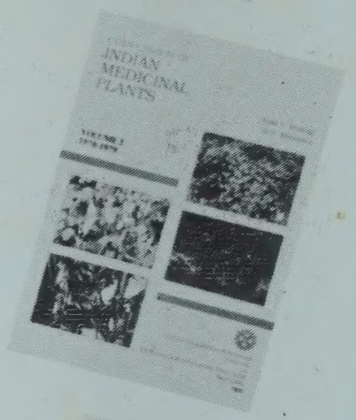

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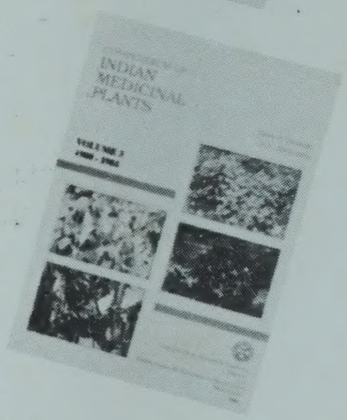

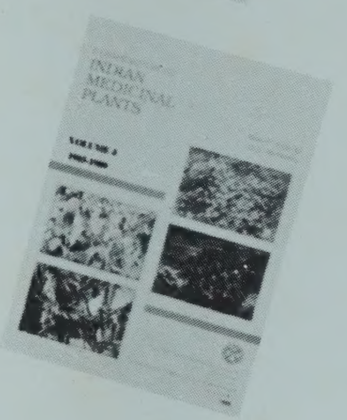

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Journal of Scientific & Industrial Research

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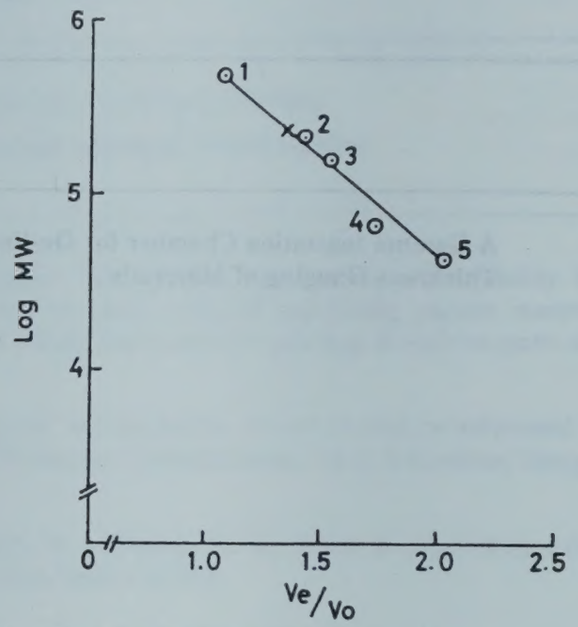
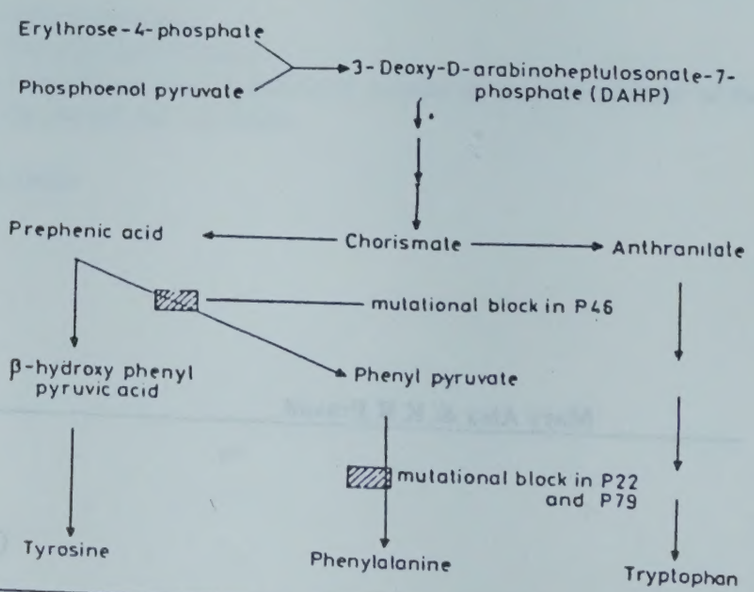
Papers

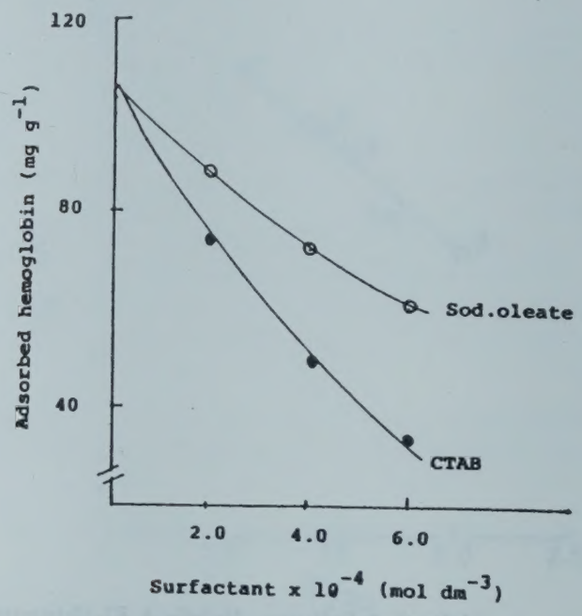
An alternate procedure for producing fructose syrup by enzymatic hydrolysis of inulin which is a fructose polymer and is stored as a reserve carbohydrate in many plants is described. It is found that purified preparation produces fructose as the only product from inulin indicating that inulinase has primarily exo mode of action. Inulinase from *A.versicolor* because of its high temperature optima and stability towards heat hydrolyses inulin at higher temperature with ease and is found to be suitabile for industrial exploitation.



Many phenylalanine axotrophic and 3-nitrotyrosine resistant mutants isolated by UV treatment of a glutamic acid producing strain of *Arthrobacter globiformis* are found to excrete tyrosine alone in glucose-NH_4Cl mineral salt medium. Among the twenty-two carbon sources tested, glucose is found to be the best and optimum glucose concentration for L-tyrosine production being 400 mM. Among fourteen different inorganic and organic nitrogen sources tested, NH_4Cl is the best and is optimum for L-tyrosine production at 60 mM.



The kinetics of the adsorption of hemoglobin onto the ACF surfaces from the alkaliane solution of the protein is studied at room temperature. Various adsorption and kinetic parameters such as the adsorption coefficient, rate constants for the adsorption and desorption, diffusion constants and penetration rate constants are calculated under varying experimental conditions. The effects of surfactants, solvents and temperature on the adsorption of hemoglobin are investigated. Various thermodynamic parameters are also evaluated.



Conference Report

The Thirteenth National Symposium on Catalysis coinciding with the Silver Jubilee of the Catalysis Society of India (CSI) held at Indian Institute of Petroleum, Dehradun during 2-4 April 1997 covers almost all aspects of Science and Technology of Catalysis. The special emphasis has been on the novel applications in applied catalysis related to petroleum refining, petrochemical speciality and fine chemicals, and the enviroment. The Symposium also includes areas such as natural gas conversion, novel materials, reaction engineering, and structure-activity relationship.

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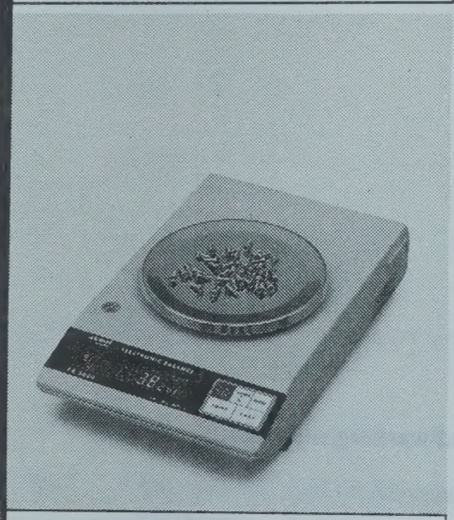

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A Gamma Ionization Chamber for On-line Thickness Gauging of Materials

Mary Alex and K R Prasad

Electronics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Received: 22 April 1997; accepted: 28 July 1997

An all-welded ion chamber with 2mm thick aluminium end-window and filled with xenon gas at four atmospheres has been developed as a replacement for an imported device. The chamber has been used in thickness gauging applications as a non-contact device in the cold rolling operation of steel and aluminium sheet material with a gamma emitting Am-241 source. The present chamber has an electrically grounded outer housing. To provide aluminium window to the stainless steel (SS) outer housing, explosion welded SS-Al clad material has been used. The chamber is operated at 800V and has a current sensitivity of 110nA/r/h and can detect changes in thickness with an accuracy of 2μ . Tests with various absorbers show that the performance is comparable to that of FAG ion chamber Type No. 41539/6010 made by M/s FAG Kugelfischer Georg Schaffer KGaA, Germany that has a 50μ thick titanium window.

Introduction

Nucleonic thickness gauges are commonly used as non-contact transmission type devices in the on-line processing of rolled steel strips. Nuclear gauges are superior to other gauges by virtue of greater accuracy in measurement and also by being more economical. In India, there is an increasing need for automation and radioisotope based gauges are being used in a variety of industries for sheet metal thickness measurement and other applications.[1] Non-contact nucleonic thickness gauges employing ionization chamber detectors and gamma sources have been described in literature.[2-4] While beta sources and X-rays are employed in a variety of applications, gamma sources are employed in the case of metal sheets of thickness up to 800kg/m^2, which corresponds to about 10mm of stainless steel.

The system developed originally at the Electronics Corporation of India Limited, Hyderabad consisted of an ion chamber filled with xenon at six atmospheres (Type 41539/6010 made by M/s FAG Kugelfischer George Schaffer KGaA, Germany) that had a 50μ thick titanium window. It was observed that the gas leaks out after some years of operation and requires refilling. The manufacturer's quotation for refilling and repair of the ion chamber proved to be uneconomical. The probability of gas leaks developing in future could not be ruled out either. It was therefore decided to develop all-welded ion chambers of comparable sensitivity with identical external dimensions for future thickness gauges. It is expected that in the present design, the gas will be permanently sealed in, ensuring long life. The present paper describes the design and performance of the prototype ion chamber developed in Electronics Division, BARC.

Description of the System

The system consists of a radiation source in a lead shield and a radiation detector which forms the measuring head in the form of a 'C' frame (Figure 1). This can be considered an enlarged and non-contact version of a micrometer screw gauge. The detector is an ion chamber mounted in the upper arm of the frame while the source holder with a 90GBq Americium-241 source (450 y half-life) is mounted on the lower arm. The source to detector distance can be varied from 150 to 400 mm. Steel sheet under cold rolling operation passes between the source and detector at a speed that varies from 200 to 500 m/min. The intensity of the radiation directed at the detector

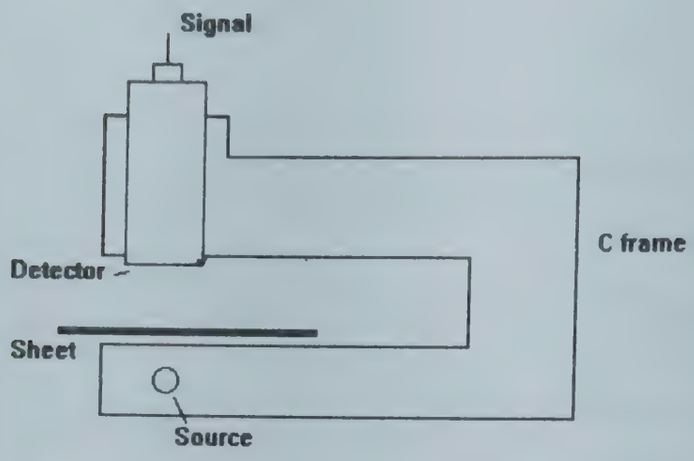

Fig. 1 — Schematic diagram of thickness gauge

above the strip is attenuated by the strip and modifies the electrical output of the detector.

A strip of thickness d placed between the source and the detector reduces the incident intensity I_0 to a value I such that $I = I_0 e^{\mu d}$ where μ is the total linear attenuation coefficient. The system can be used to measure steel strip thicknesses up to 6mm with an accuracy of 0.5 per cent. The detector signal is electronically processed on-line to display and give suitable outputs for process control. Any deviation from a preset value is used for feedback control so that the correct sheet thickness is maintained.

Ion Chamber Design

Figure 2 shows the schematic diagram of the imported chamber where voltage was applied to the outer housing. A special triax type ceramic insulator, segmented by an electrically grounded guard ring, was used to isolate the collecting electrode from the outer housing. (The use of such an insulator is necessary to prevent the flow of leakage current across the insulator surface into the signal circuit). The insulator flange was soldered to the chamber housing. The chamber was filled with xenon gas at six atmospheres and the titanium end-window was kept in place with the help on an O-ring seal and screws.

In the present design (Figure 3), the outer housing is electrically grounded and connections to the high tension (HT) and collecting electrodes are provided by means of alumina-metal feedthrough insulators that give insulation of the order of 10^{14} ohms and withstand filling pressures up to 1000psi. Separate insulators for the electrodes have been employed because of the difficulty and expense involved in procuring a weldable ceramic- metal triax type insulator. The chamber base-plate and housing were also made of SS to facilitate the welding of the SS conductor of the alumina-metal feedthrough insulators. Since the chamber has to detect 60keV gammas emitted by the Am-241 source, and since titanium can not be welded to SS, it was decided to provide an aluminium end-window. The end-window was fashioned out of explosion-welded SS-Al clad material obtained from the Explosives Research and Development Laboratory, Pune. Explosion welding is a process for bonding two dissimilar metals like SS and aluminium which can not be welded by conventional methods.[5] The bonding is not affected by subsequent operations like machining and welding that are carried out on the clad plate. Figure 4 shows the welding

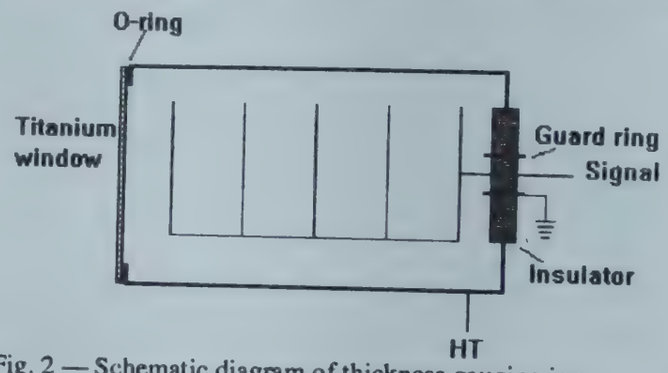

Fig. 2 — Schematic diagram of thickness gauging ion chamber with titanium window (50μ)

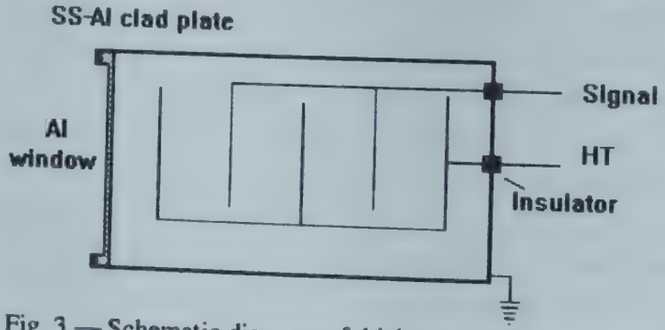

Fig. 3 — Schematic diagram of thickness gauging ion chamber with 2mm aluminium window

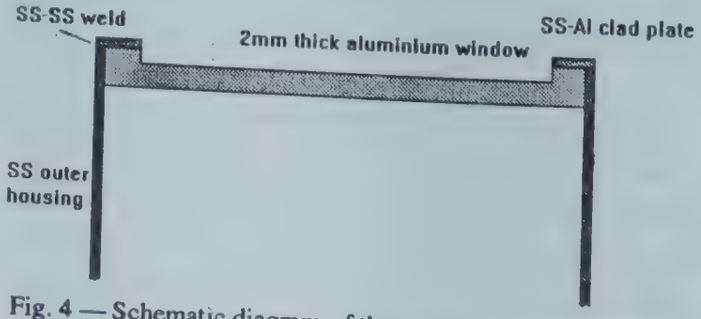

Fig. 4 — Schematic diagram of the welding detail of the SS-Al clad plate used as end window for thickness gauging ion chamber

detail. Two sets of parallel plate electrodes, with their supports mounted on high purity alumina bushings, have been used as the HT and collecting electrodes. 1.25mm thick aluminium plates (3 numbers for HT and 2 numbers for collector spaced 15mm apart) have been used for the electrodes. The chamber has been filled with 99.9995per cent pure xenon gas at four atmospheres that can be withstood by the aluminium window. The chamber is operated at 800V.

Tests and Results

The reduction in the sensitive volume, the use of 2mm aluminium instead of 0.05mm thick titanium window and the lower filling pressure have all contributed to a decrease in the current sensitivity of the present chamber. While the original FAG chamber has a sensitivity of 160nA/r/h, the BARC chamber, calibrated with Am-241 gamma source, has a sensitivity of 110nA/r/h. Figures 5, 6 and 7 show the readings from a working chamber manufactured by M/s FAG comparison with the BARC chamber. Table 1 shows the readings taken by the users at ECIL from the BARC ion chamber.

Conclusion

Tests at ECIL have shown that the present chamber can be used as a thickness gauge instruments as an alternative to the original ion chamber and the decrease in sensitivity is acceptable. Users have reported that the present chamber can measure thicknesses with an accuracy of 2μ. We are looking into the possibility of using SS-Al clad plate fused by diffusion process[6] as an alternative to the explosion-welding process. About 15 such devices will be required every year and it is expected that a substan-

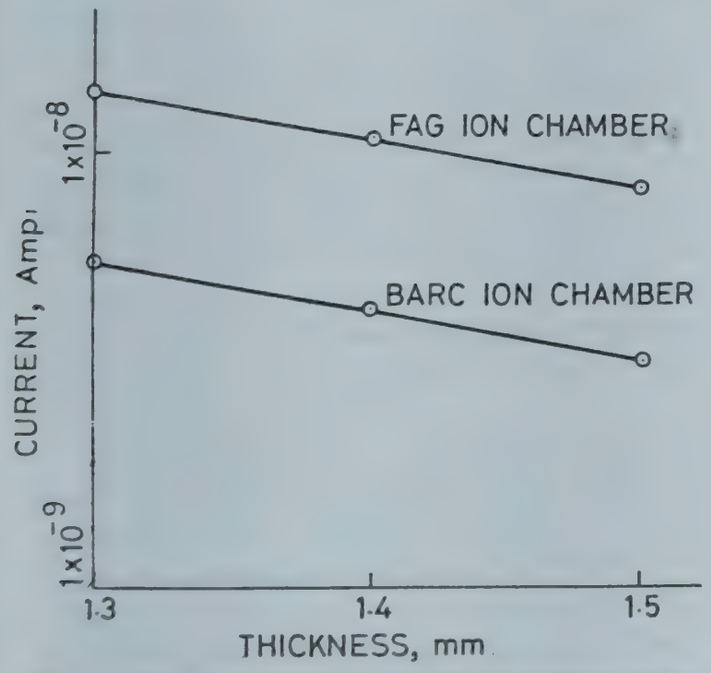

Fig. 5 — Thickness gauging ion chamber signal change with S-S absorber

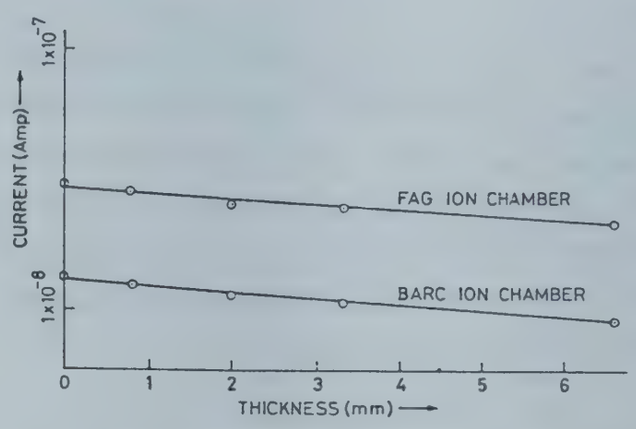

Fig. 6 — Thickness gauging ion chamber signal change with Al absorber

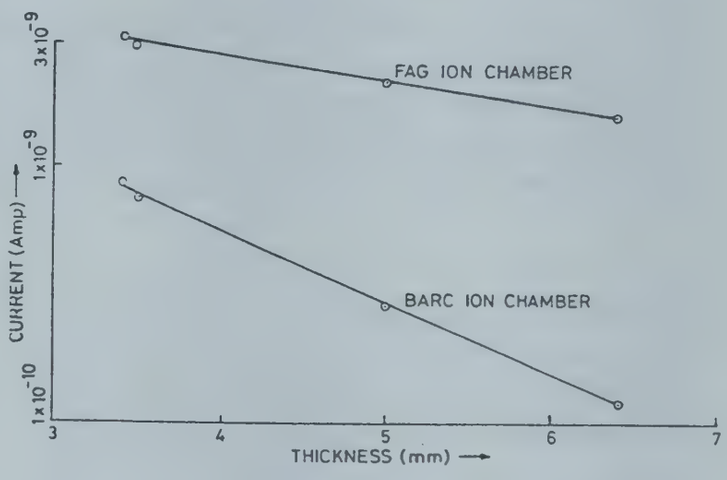

Fig. 7 — Thickness gauging ion chamber signal change with MS absorber

Table 1 — Results of tests carried out at ECIL on thickness gauging ion chamber developed in BARC

Absorber material	Thickness (μ)	Ion chamber signal (V)
Cooper	52	8.967
	450	5.223
	1260	1.693
Brass	64	8.901
	540	4.553
	1680	1.017

tial amount of foreign exchange will be saved through indigenous development of thickness gauging ion chambers.

Acknowledgement

The authors are thankful to Head, Electronics Division, Bhabha Atomic Research Centre, Mumbai for encouraging and supporting the development work and to Dr S A Khayyoom, Deputy General Manager, Instruments Group, Marketing in the ECIL, Hyderabad and his colleagues for making available test results on the ion chamber. Thanks are also due to Director, ERDL, Pune, and his colleagues for providing the clad material.

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Vol. 56, December 1997, pp 721 - 726

Inulinase from *Aspergillus versicolor*: A Potent Enzyme for Producing Fructose from Inulin

Anuradha Kochhar, Narinder Kaur and Anil K Gupta*

Department of Biochemistry, Punjab Agricultural University, Ludhiana 141 004, India

Received: 20 June 1997; accepted: 27 August 1997

An alternate procedure for producing fructose syrup is by enzymatic hydrolysis of inulin which is a fructose polymer and is stored as a reserve carbohydrate in many plants. For achieving the objective of having high inulinase producing organism, various fungal species were screened for the production of extracellular inulinase. *Aspergillus versicolor* (MTCC 280) produced about 14 units of inulinase ml^{-1} of medium after 15 d of growth. The inulinase was purified by over 50-folds by ammonium sulphate fractionation, DEAE cellulose, CM cellulose and sephadex G 150 column chromatographies. Invertase to inulinase ratio of one in culture filtrate was reduced to 0.7 in the purified preparation. The pH and temperature optima were 5.5, and 55 to 60°C, respectively. The molecular weight of inulinase was determined as 230±20Kd. Michaelis constant (*K*m) of inulinase with inulin as substrate was 0.12 m*M*. The purified preparation produced fructose as the only product from inulin indicating that inulinase has primarily exo mode of action. Enzyme was considerably stable to heat and 1h heating at 60°C caused only 15 to 20 per cent loss of activity. Inulinase from *A. versicolor* because of its high temperature optima and stability towards heat could hydrolyse inulin at higher temperature with ease and appeared to be suitable for industrial exploitation. Enzyme was inhibited non- competitively by $HgCl_2$ having dissociation constant of enzyme-inhibitor complex(Ki) of 0.2μM .

Introduction

The use of sucrose as a sweetener is facing competition from fructose syrup because of its medicinal and nutritional properties . Fructose syrup has gained importance as an alternative to sucrose because the latter is known to cause problems related to corpulence, cariogenicity, atherosclerosis and diabetes[1], whereas fructose has beneficial effects in diabetic patients, increases the iron absorption in children and has a higher sweetening capacity so it can be used in the diet of obese persons[2].

Conventional method of producing fructose is based on amylolysis of starch with amylase and amyloglucosidase followed by glucose isomerase catalysed conversion of glucose to fructose. The fructose's yield by this method is about 45 per cent, rest being glucose (50 per cent), and oligosaccharides (8 per cent). Though, ion exchange chromatography techniques have been developed for enrichment of fructose but these techniques add to the cost of production[3]. Direct production of fructose from fructose polymer inulin by inulinase can give 90 per cent yield of fructose by a single step reaction. This fructose polymer is abundantly present in roots of *Cichorium intybus*[4]. Because of low solubility of inulin at room temperature, a thermally stable inulinase with high temperature optima is required for any industrially acceptable preparation[5]. Here, we report the properties of a highly stable inulinase with high optimum temperature for its action from *Aspergillus versicolor*.

* For correspondence

Experimental

Fungal strains were obtained either from National Chemical Laboratory, Pune or from Institute of Microbial Technology, Chandigarh. Seeds of chicory (*Cichorium intybus* var. Kalpa No 1) were sown in the field in the first week of November and roots

harvested in April. Inulin was precipitated from the aqueous extract of chicory roots with ethanol and purified and dried as described earlier[6]. Fungal strains were maintained in an agar based sterilised medium[7]. The spores from agar-based slants were inoculated in to 50 ml of liquid medium in 250 ml conical flasks. The flasks were incubated at 30°C on a rotary shaker (250 rev min^{-1}) for 3 d . This inoculum (1ml) was used for inoculating the medium containing 2 per cent (W/V) inulin instead of glucose as carbon source.

Activities of inulinase and invertase were determined from the culture filtrates obtained at different days of growth after centrifuging at 10000 g for 15 min at 4°C . The supernatants were eluted through sephadex G-25 column using 50 m*M* sodium acetate buffer (pH 5.4) to remove reducing sugars and effluents so obtained were used for assaying inulinase and invertase activities[8]. The assay system consisted of 0.1 ml of enzyme preparation and 0.9 ml of 1.1 per cent inulin (2 μ mol approx.) in 0.1 *M* sodium acetate buffer (pH 5.4). For measuring sucrose hydrolytic activity, inulin was replaced by 0.9 ml of 55.5 m*M* sucrose. The contents were incubated for 20 to 30 min and formation of products was quantified[8]. One inulinase unit is the quantity of enzyme which produces 1μmol of fructose min^{-1} under assay conditions. One invertase unit is the quantity of the enzyme which hydrolyses 1 μ mol of sucrose min^{-1} under assay conditions.

Inulinase was purified from culture filtrate of *A. versicolor* obtained after 15 d of growth. The culture filtrate was centrifuged at 10000 g at 4°C and inulinase was precipitated by differential ammonium sulphate fractionation. The precipitates obtained with 60 to 100 per cent ammonium sulphate saturation were dissolved in minimum volume of 0.1 *M* sodium phosphate buffer (pH 7.0) and inulinase was passed through sephadex G-25 column to remove sulphate ions. This preparation was loaded on DEAE cellulose column and enzyme was eluted by 20 m*M* sodium phosphate buffer (pH 7.0). Enzyme was further purified by CM cellulose and sephadex G-150 column chromatographies. The protein content was estimated by the procedure of Lowry *et al*[9].

The molecular weight (MW) of inulinase was determined by measuring its elution volume (Ve) on sephadex G-150 column. Apoferritin (440 Kd), β-amylase (200 Kd), alcohol dehydrogenase (150 Kd), bovine serum albumin (66 Kd), and carbonic anhydrase (29 Kd) were used as markers of MW. The void volume (*Vo*) of sephadex G-150 column was determined by eluting blue dextran. The log MW of different proteins was plotted against *Ve*/*Vo* to determine the MW of inulinase.

Results and Discussion

Aspergillus versicolor (MTCC 280) was selected for the present study after screening several fungal strains for their capacity to synthesise extracellular inulinase after growing on inulin based growth medium. In an effort to increase the synthesis of inulinase, effect of different nitrogen sources on the level of extracellular inulinase in the medium on different days of growth was studied (Table 1). Maximum yield of inulinase of about 14 units ml^{-1} of medium was obtained on addition of 0.2 per cent ammonium dihydrogen phosphate and 0.15 per cent sodium nitrate after 15 d of fungal growth. However, these nitrogen sources were not effective in enhancing inulinase activity when added individually in the medium. With glycine and urea as the nitrogen sources, the inulinase production was about 10 units ml^{-1} of the medium (Table 1). Gupta *et al.*[6] have reported increased production of inulinase with sodium nitrate as a nitrogen source in the medium of *Fusarium oxysporum*, whereas it exerted an inhibitory effect on inulinase production in *Kluyveromyces fragilis*[10]. Derycke and Vandamme[7] have reported stimulation of inulinase production by *Aspergillus niger* on addition of ammonium dihydrogen phosphate . It appears that each fungal species has preference for a specific nitrogen source for optimum production of inulinase.

The precipitation of inulinase by adding two volumes of chilled ethanol in the medium could precipitate only 10 per cent of the activity after overnight ageing at 0°C. By employing differential ammonium sulphate fractionation, the major inulinase activity could be precipitated with 60 to 100 per cent salt saturation. After removal of sulphate ions by sephadex G-25 chromatography, the 60 to 100 per cent ammonium sulphate fraction was loaded on DEAE cellulose column. Inulinase was not held up by the DEAE cellulose and was eluted with 20 m*M* sodium phosphate buffer (pH 7.0) before applying

the sodium chloride gradient. Even on CM cellulose, the enzyme was weakly bound and was eluted just before the application of sodium chloride gradient. It might be possible that inulinase of *A. versicolor* has isoelectric point near 6 to 7 pH and is, therefore, not withheld by ion exchangers around this pH. The pooled fractions obtained from CM cellulose column were passed through sephadex G-150 column giving only one peak of inulinase. Maximum specific activity of inulinase of 650 units mg^{-1} protein was obtained in fraction 19 which was about 54-folds higher than that of crude extract. Overall summary of purification data has been presented in Table 2. However, for kinetic studies fractions 15 to 20 obtained after gel filtration chromatography were pooled.

The purified fractions in addition to inulinase activity also contained some sucrose hydrolytic activity. The invertase to inulinase activity ratio (S/I) which was about one in the crude extract was reduced to 0.7 in the purified fraction. According to Vandamme and Derycke[1], true inulinase has S/I ratio less than 10, whereas a true invertase has a S/I ratio of about 5000 . As per this definition, *A. versicolor* produced a true inulinase. It is now an accepted fact

Table 1 — Effect of different nitrogen sources in the medium on the production of extracellular inulinase during growth of *A. versicolor*

Nitrogen source (0.35 per cent)	Inulinase units ml^{-1} of medium after growth (d)			
	5	10	15	20
0.2 per cent $NH_4H_2PO_4$ +0.15 per cent $NaNO_3$	3.9	11.8	14.3	7.9
$NH_4H_2PO_4$	0.2	0.8	3.7	0.3
Glycine	2.6	9.1	10.7	6.4
Malt extract	0.2	9.4	3.0	0.3
Peptone	0.2	0.3	3.7	1.0
$NaNO_3$	0.2	0.4	2.7	1.0
Urea	1.6	6.4	10.7	5.5

Values are means of data obtained from samples of three different flasks.

Table 2 — A summary of the data on the purification of inulinase from *A. versicolor*

Fraction	Enzyme units	Specific activity (Units mg^{-1} protein)	Purification Fold
Crude extract	326.8	12	1.0
Sephadex G 25	297.1	27	2.2
60 to 100 per cent $(NH_4)_2SO_4$ saturation	140.1	35	2.9
DEAE cellulose (Fraction 4 to 7)	102.6	102	8.5
CM cellulose (Fractions 8 to 11)	72.0	120	10.0
Sephadex G 150 (Fractions)			
15	4.4	176	14.6
16	7.0	233	19.4
17	7.0	280	23.3
18	8.5	340	28.3
19	7.9	658	54.8
20	4.5	180	15.0

Fractions of 5 ml each were collected during various column chromatographies. In ion exchange chromatography, linear gradient of NaCl was applied after 50 ml of eluting buffer. The void volume of sephadex G 150 column was 58 ml.

that inulinase purified from various sources after number of chromatographic processes possesses some sucrose hydrolytic activity[8,11]. These workers[8,11] suggested that the active site of inulinase might have two parts: one being involved in sucrose hydrolysis and other in inulin hydrolysis. The proposal that sucrose and inulin hydrolytic activities might be due to same enzymes got support from the observations that both activities have similar response to thermal denaturation (Table 3).

Effect of increasing time of incubation on inulinase activity was studied at different temperatures. Up to 1 h of incubation, the optimum temperature of inulinase was 60°C. However, if incubation time of the assay system was increased from 1 h to 2 to 3 h the optimum temperature changed to 55°C. Obviously this may be due to some denaturation of enzyme at 60°C on prolonged incubation. The product formation was linear for at least 2 h at 55°C (Table 4).

The pH optima of inulinase was 5.5. The data can be compared with pH optima of 4.4, 4.6, and 6.0 for inulinases from *A.niger*[7], *Clostridium acetobutylicum*[12], and *Fusarium oxysporum*[13].

Using velocity data obtained with increasing concentrations of inulin in the assay system, Michaelis constant (*K*m) of inulinase, as determined by Lineweaver-Burk and velocity vs substrate concentration graphs was about 0.12 m*M*. The inulinae showed hyperbolic increase in activity with increasing inulin concentration. The *K*m of inulinase of *A.versicolor* can be compared with the *K*m values of 17 m*M* from *Candida salmenticensis*[14], 15 m*M* from *Debaryomyces contarelli*[15], and less than 1 m*M* from *Fusarium oxysporum*[6].

Molecular weight of purified inulinase was determined to be about 230+20Kd (Fig. 1). Lot of variation in molecular weights of inulinase from *Aspergillus* species has been reported in literature. Inulinase from *Aspergillus niger* has a molecular weight of 300 Kd, whereas inulinase from *Aspergillus ficuum* and other *Aspergillus* species have a MW between 43 Kd to 81 Kd[11,17,18].

To understand the possible mechanism of action of inulinase on inulin, the samples were taken from the reaction mixture after 1, 2, and 3 h incubation. Fructose was identified as the only product of inulinase action by paper partition chromatography. These results indicate that inulinase of *A.versicolor* has primarily an exo mode of action on inulin. In the case of endo- inulinase, the products of inulin hydrolysis are mixture of oligosaccharides.

Out of various cations like Ba^{2+}, Ca^{2+}, Mn^{2+}, Mg^{2+}, and Hg^{2+} at 5 m*M* concentration, only Hg^{2+} caused complete inhibition, whereas others had no effect.

Table 3 — Thermal stability of partially purified inulinase from *A.versicolor*

Temperature (°C)	Per cent loss of activity after heating for 1 h	
	Inulin hydrolytic activity	Sucrose hydrolytic activity
40	0	0
50	0	0
60	16.7	20.0
70	63.3	70.4

Enzyme was pre-incubated at different temperatures for 1 h before measuring the activity. The control was not pre-incubated and its activity was considered as 100. The per cent remaining activity was subtracted from 100 to calculate per cent loss of activity. Data represents mean of two assays.

Table 4 — Effect of incubation time and temperature on activity of inulinase

Incubation time (min)	µmol of fructose produced ml^{-1} enzyme at °C					
	37	45	50	55	60	65
30	21.8	27.1	33.9	36.1	44.0	32.1
60	43.9	53.7	63.4	70.5	76.2	48.2
120	75.8	92.5	127.8	147.1	115.4	67.4
180	105.3	132.6	174.5	190.3	166.2	82.0

Data are mean of triplicate assays

From the Dixon's graph (Fig. 2), Hg^{2+} was found to be the non-competitive inhibitor with dissociation constant of enzyme-inhibitor complex (Ki) of 0.2 μM.

Inulin has only about 1.5 per cent solubility at 30°C, whereas at 60°C inulin solubility is about 10 per cent[5]. Because of low solubility of inulin at low temperature, for efficient hydrolysis of inulin, an inulinase with high optimum temperature and good thermal stability is required. Inulinase from *A.versicolor* fulfills these high demanding criteria and has the potential to be used in the industry provided large amount of this enzyme could be made available either by further mutating this organism or by increasing the copies of the gene of this enzyme or by introducing number of genes in some fast growing organism.

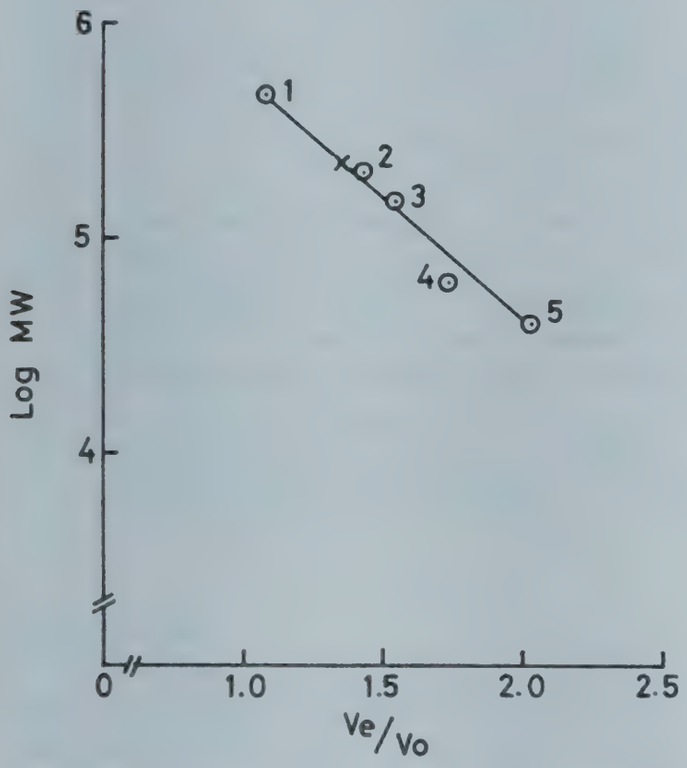

Fig. 1 — Determination of MW of inulinase by sephadex G 150 column chromatography: (1) apoferritin (440 Kd); (2) β-amylase (220 Kd); (3) alcohol dehydrogenase (150 Kd); (4) BSA (66Kd); (5) carbonic anhydrase (29Kd) and *purified inulinase

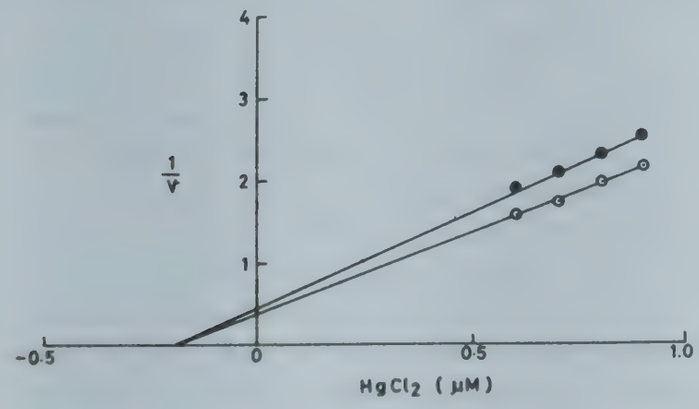

Fig. 2 — Dixon graph showing non-competitive inhibition of inulinase. Inulin concentration :• ----•, 0.2 mM and 0----0, 1.0 mM

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Production of Tyrosine by Auxotrophic and Analogue Resistant Mutants of *Arthrobacter globiformis*

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Many phenylalanine auxotrophic and 3-nitrotyrosine resistant mutants isolated by UV treatment of a glutamic acid producing strain of *Arthrobacter globiformis* were found to excrete tyrosine alone in glucose-NH_4Cl, mineral salt medium. Among the twentytwo carbon sources tested, glucose was found to be the best and optimum glucose concentration for L-tyrosine production was 400 mM. Among fourteen different inorganic and organic nitrogen sources tested, NH_4Cl was found to be the best and was optimum for L-tyrosine production at 60 mM. Phenylalanine for L-tyrosine production was optimum at 50 $\mu g\ ml^{-1}$. On the optimum level of C, N and phenylalanine, a yield of 2.384 $g\ l^{-1}$ L-tyrosine was achieved from a 3-nitrotyrosine resistant mutant $P_{46}NT_E$, among the twelve nitrotyrosine resistant mutants isolated following UV-irradiation.

Introduction

Among the aromatic aminoacids, L-tyrosine is used as a therapeutic agent, for improving taste of food and as a laboratory reagent. Addition of phenylalanine and L-tyrosine brings about a marked change in taste of champagne. It has also been observed that L-tyrosine promotes growth of various vegetables when used together with kinetin[1]. The therapeutic use of 3,4-dihydroxy L-phenylalanine (L-DOPA) for Parkinson disease[2] has increased the demand for L-tyrosine as a raw material. L- Tyrosine is also used as a component for suntan oil[3]. As a result, demand for overproduction of L-tyrosine is gradually increasing. After the work of Kinoshita *et al.*[4], microbial production of amino acids has received considerable attention in the fermentation industry. Though various chemical, biotransformational, and direct fermentation methods have been used to produce L-tyrosine, significant success for low cost production of L-tyrosine has been achieved by using auxotrophic mutants of bacteria. L-Tyrosine production has been reported with auxotrophic and analogue resistant mutants of *Corynebacterium glutamicum*[5,6], *Bacillus subtilis*[7,8], *Brevibacterium lactofermentum*[9], *E. coli*[10], *Methylomonas* sp.[11,12], *Salmonella typhimurium*[13]. The present paper describes the suitability of different C and N sources and their optimal level of L-tyrosine production by auxotrophic analogue resistant mutant strains of *Arthrobacter globiformis*.

Materials and Methods

Organism, Media and Growth Condition — The glutamate producing strain *A. globiformis* was isolated from a soil sample of Burdwan town, West Bengal by Roy and Chatterjee[14] and maintained on Alfoldi's agar slant[15] at 10°C in refrigerator with periodic transfer to fresh slants. A mutant which is phenylalanine auxotroph and resistant to 3-nitrotyrosine (an analogue of tyrosine) derived from a prototrophic strain of *A. globiformis* by two step mutagenesis with ultra violate radiation[16]. These mutants were grown in Alfoldi's broth[15] supplemented with required amount of phenylalanine and 3- nitrotyrosine on a rotary shaker at 30°C. Cell growth was determined terbidometrically in an EEL (UK) colorimeter at 540 nm.

Analytical Method — Tyrosine excreted in the agar plate was detected by cross streak assay using tyrosine auxotroph. Quantitative estimation of L-ty-

rosine was done colorimetrically after paper chromatographic separation as well as by microbiological assay using a tyrosine auxotrophic strain of *A. globiformis*.

Results and Discussion

Detection of the Site of the Mutational Block in Phenylalanine Biosynthetic Pathway of the Tyrosine Excreting Phenylalanine Auxotrophs

For the detection of mutational block in the phenylalanine biosynthesis pathway, both liquid and agar medium of Alfoldi's were used. Six different combinations of amino acids and their available precursor were supplemented to the liquid medium and agar plate. All supplemented media were inoculated with different phenylalanine auxotrophs (P_{46}, P_{22} and P_{79}), incubated separately for 72h at 30°C and observed for growth. The results (Table 1) indicate that all the single auxotroph require phenylalanine. The auxotroph P_{46} was able to grow in the minimal medium supplemented with phenylalanine and phenylpyruvic acid but P_{22} and P_{79} failed to grow in phenylpyruvic acid. So in the case of strain P_{46}, mutational metabolic block in phenylalanine pathway occurred between prephenic acid and phenylpyruvic acid. But in the case of strain P_{22} and P_{79} the mutational block occurs in between phenyl pyruvic acid and phenylalanine production (Fig.1).

Table 1 — Detection of the site of mutational block in the tyrosine biosynthetic pathway

Medium supplemented with amino acid and amino acid precursor	Mutant strain		
	P_{46}	P_{22}	P_{79}
Minimal (No amino acid added)	—	—	—
Minimal +Tyrosine	—	—	—
Minimal +Tryptophan	—	—	—
Minimal +Phenylalanine	+	+	+
Minimal +Prephenic acid	+	—	—
Minimal +Phenylpyruvic acid	+	—	—

Note: +=Growth, — =No growth

Suitability of Different Basal Media for Growth and Tyrosine Production

In order to find a suitable basal medium for tyrosine production, minimal salt media studied by Alfoldi's[15], Davis[17], Robinson[18], Tanaka[19] and Tokoro *et al.*[20] were tested. All the above media contained one per cent glucose (w/v) as carbon source. The prototroph and three phenylalanine auxotrophs could grow in all the above five synthetic media tested (Table 2). Alfoldi's medium was found to be most suitable for growth and phenylalanine production. Media of Davis[17] and Robinson and Tokoro *et al.*[20] though suitable for cell growth but were not suitable for tyrosine production. The medium of Tanaka showed poor growth and tyrosine production. Alfoldi's medium was, therefore, selected as a basal medium for further optimization experiments.

Suitability of Different Carbon Sources

In order to find out a suitable C source, several C sources including sugars, sodium salts of many organic acids, polyalcohols and polysaccharides were tested at two per cent level. The C sources were sterilized separately and added into the broth medium. The final pH of the medium was adjusted to 7.0. Phenylalanine was added at 25μg ml^{-1}. The flasks in triplicate for each C source were inoculated

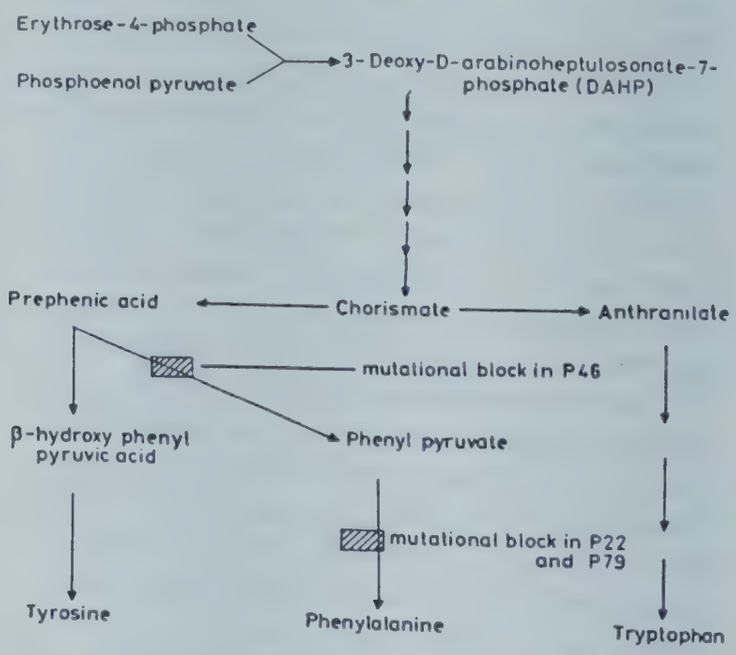

Fig. 1 — Site of mutational block in phenylalanine biosynthetic pathway of *A. globiformis* single auxotrophs

with suspension of washed bacterial cells from 24h old slant culture and incubated on a rotary shaker at 30 ± 1°C for 72 h. From Table 3, it is evident that among the different C sources tested, glucose and fructose were suitable for both growth and tyrosine production. Among the disaccharides, sucrose was most suitable for the purpose. Except glycerol, the

Table 2 — Suitability of different basal media for growth and tyrosine production

Medium used	Strain							
	Wild		P_{46}		P_{22}		P_{79}	
	Growth[a]	Tyrosine[b]	Growth	Tyrosine	Growth	Tyrosine	Growth	Tyrosine
Alfoldi's	3.2	0.11	2.8	0.26	2.6	0.22	2.8	0.23
Tanaka	0.7	—	0.6	—	0.6	—	0.5	—
Tokoro	3.6	0.05	2.6	0.11	2.5	0.12	2.8	0.11
Davis	3.1	0.03	2.1	0.11	2.2	0.13	2.1	0.11
Robinson	2.9	0.04	2.1	0.01	2.1	0.12	2.1	0.12

Note: a =OD in EEL unit, b =g l^{-1}, — =trace

Table 3 — Suitable carbon source for tyrosine production

Name of the carbon source[a]	Strain					
	P_{46}		P_{22}		P_{79}	
	Growth[b]	Tyrosine[c]	Growth	Tyrosine	Growth	Tyrosine
Glucose	3.5	0.41	3.6	0.32	3.5	0.33
Fructose	3.3	0.34	3.5	0.31	3.6	0.31
L(+) Arabinose	3.1	0.32	3	0.26	3.1	0.25
L(+) Galactose	2.6	0.29	2.6	0.21	2.5	0.21
D(+) Mannose	0.2	—	0.3	—	0.2	—
D(+) Ribose	2.9	0.33	2.9	0.32	3	0.29
Rhamnose	0.4	Trace	0.3	—	0.3	—
Amygdalin	0.5	—	0.4	—	0.4	—
Lactose	3.2	0.33	3.1	0.29	3.2	0.31
Maltose	3.5	0.33	3.5	0.30	3.5	0.3
Sucrose	3.4	0.33	3.5	0.29	3.5	0.3
Cellobiose	1.6	0.16	1.7	0.09	1.6	0.15
Mannitol	3.2	0.15	3.3	0.13	3.2	0.14
m-inositol	2.4	0.09	2.4	0.08	2.5	0.09
Glycerol	3.1	0.14	3.1	0.13	3.2	0.13
Starch	3.4	0.17	3.3	0.15	3.4	0.16
Glycogen	2.9	0.11	2.9	0.12	3.1	0.11
Na-citrate	2.4	0.12	2.4	0.13	2.5	0.14
Na-Fumarate	2.3	—	2.2	—	2.3	—
Na-glycerophosphate	2.5	—	2.5	—	2.5	—
Na-succinate	2.1	0.04	2.4	0.1	2.2	0.11
Molasses	3.5	0.33	3.5	0.3	3.6	0.31

Note: a =2% (w/v), b =OD in EEL unit, c =g l^{-1}, — =trace

sugar alcohols were unsuitable. Sodium salts of various organic acids tested were found to be unsuitable. Molasses was suitable only next to glucose and fructose. Similar observations of glucose to be most suitable C source for tyrosine production have been reported with *Brevibacterium flavum*[21], *Corynebacterium glutamicum 13032*[7,8]. However, for 2-thienylalanine and phenylalanine hydroxymate resistant mutants of *Methylomonas* sp.[11,12], and *Corynebacterium glutamicum KY10233*[6], methanol and cane molasses, respectively, were found to be most suitable.

Optimum Concentration of Glucose for Tyrosine Production

Earlier experiments have shown glucose to be the best carbon source for L-tyrosine production. To find out the optimal level of glucose, different concentration, viz. 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600 mM were tested and 400 mM was found to be the best (Table 4) for growth and L-tyrosine production for all the three phenylalanine auxotrophs. Above this level, both growth and L-tyrosine production decrease. The mutant P_{46} accumulated the highest amount of L-tyrosine at the optimum level of glucose in the growth medium.

Suitability of Different N Sources

For suitability of different nitrogen sources, many different organic and inorganic compounds, viz. $(NH_4)_2SO_4$, NH_4Cl, NH_4NO_3, L-asparagine, L-alanine, L-glutamic acid, CH_4N_2O, L-tryptophan, L-serine, KNO_3, $NH_4C_2H_3O_2$, $(NH_4)H_2PO_4$, $C_2H_8N_2O_4.H_2O$ were tested at 40mM level. From the results (Table 5), it is evident that NH_4Cl and NH_4NO_3 are the most suitable N source for L-tyrosine production. Next, in order of suitability for L-tyrosine production were KNO_3, L-asparagine, L-alanine, $(NH_4)_2SO_4$, glutamic acid and CH_4N_2O. $C_2H_8N_2O_4.H_2O$, $NH_4C_2H_3O_2$, tryptophan and phenylalanine were not found to be suitable for growth and production of tyrosine.

Optimum Concentration of Suitable N Source for Tyrosine Production

In order to determine optimum concentration of NH_4Cl and NH_4NO_3, both the compounds were tested at 20, 40, 60, 80 and 100 mM level. The results (Table 6) revealed that for all the three phenylalanine mutants NH_4Cl and NH_4NO_3 were optimal at 60mM level. Ammonium sulphate was used as a suitable nitrogen source for L-tyrosine production by various organisms[5,6,22]. But in the present study NH_4Cl at 60 mM level has been found to be most suitable for tyrosine production.

Table 4 — Determination of optimum concentration of suitable carbon source

Concentration of glucose[a]	Strain					
	P_{46}		P_{22}		P_{79}	
	Growth[b]	Tyrosine[c]	Growth	Tyrosine	Growth	Tyrosine
50	2.1	0.23	2.1	0.2	2.1	0.21
100	3.4	0.42	3.5	0.34	3.4	0.34
150	3.9	0.51	3.9	0.44	3.8	0.42
200	4.2	0.54	4.3	0.51	4.2	0.51
250	4.4	0.62	4.4	0.62	4.4	0.63
300	4.5	0.71	4.6	0.71	4.6	0.72
350	4.6	0.82	4.6	0.76	4.6	0.91
400	4.9	0.91	4.8	0.88	4.9	0.84
450	4.6	0.85	4.5	0.79	4.5	0.74
500	4.4	0.83	4.4	0.75	4.4	0.74
550	4.4	0.83	4.3	0.73	4.3	0.73
600	4.2	0.81	4.2	0.71	4.3	0.73

Note: a =in mM, b =OD in EEL unit, c =g l^{-1}

Table 5 — Suitability of different nitrogen source for tyrosine production

Nitrogen sources in mM conc.	Strain					
	P_{46}		P_{22}		P_{79}	
	Growth[a]	Tyrosine[b]	Growth	Tyrosine	Growth	Tyrosine
NH_4NO_3	4.9	0.84	4.7	0.81	4.8	0.83
NH_4Cl	5.1	0.91	5.1	0.89	5.0	0.88
$(NH_4)SO_4$	4.2	0.63	4.1	0.54	4.1	0.62
$NH_4C_2H_3O_2$	0.5	Trace	0.5	Trace	0.6	Trace
$C_2H_8N_2O_4.H_2O$	1.4	Trace	1.4	Trace	1.5	Trace
$(NH_4)H_2PO_4$	1.2	Trace	1.3	Trace	1.2	Trace
L-Asparagine	3.8	0.61	3.8	0.57	3.8	0.59
α-Alanine	3.8	0.58	3.9	0.54	3.9	0.56
L-Glutamic acid	3.4	0.35	3.6	0.32	3.4	0.33
L-Serine	3.7	0.29	3.9	0.25	3.9	0.26
L-Phenylalanine	0.3	—	0.3	—	0.2	—
L-Tryoptophan	0.2	—	0.2	—	0.2	—
KNO_3	3.9	0.61	3.9	0.62	3.8	0.61
CH_4N_2O	2.2	—	2.1	—	2.1	—

Note: a =OD in EEL unit, b =g l^{-1}

Table 6 — Determination of optimum concentration of suitable nitrogen source

Nitrogen source	Conc. in mM	Strain					
		P_{46}		P_{22}		P_{79}	
		Growth[a]	Tyrosine[b]	Growth	Tyrosine	Growth	Tyrosine
	20	2.9	0.64	2.8	0.61	2.8	0.62
	40	5.1	0.84	5.2	0.82	5.1	0.83
NH_4NO_3	60	5.3	0.91	5.3	0.92	5.3	0.92
	80	5.4	0.82	5.3	0.84	5.4	0.72
	100	5.4	0.64	5.4	0.73	5.5	0.71
	20	2.8	0.72	2.9	0.71	2.9	0.72
	40	5.1	0.91	5.2	0.94	5.2	0.94
NH_4Cl	60	5.4	1.21	5.4	1.11	5.4	1.14
	80	5.5	1.14	5.4	1.04	5.5	1.03
	100	5.3	1.03	5.4	1.02	5.4	1.02

Note: a =OD in EEL unit, b =g l^{-1}.

Optimum Concentration of Phenylalanine for Tyrosine Production

To study the effect of L-phenylalanine on tyrosine production by the three phenylalanine auxotrophs, various concentrations of phenylalanine from 25 μg ml^{-1} to 150 μg ml^{-1} were tested. As shown in Table 7, at 50μg ml^{-1} concentration of L-phenylalanine and the yield of L-tyrosine by the three mutant strains was increased by about 30 per cent as compared to that at 25μg ml^{-1} concentration. Further increase in concentration of L-phenylalanine, decreased the yield up to a great extent.

Table 7 — Determination of optimum concentration of phenylalanine for tyrosine production

Phenylalanine concentration, μg ml^{-1}	Strain					
	P_{46}		P_{22}		P_{79}	
	Growth[a]	Tyrosine[b]	Growth	Tyrosine	Growth	Tyrosine
25	5.4	1.14	5.4	1.22	5.4	1.2
50	5.6	1.52	5.5	1.44	5.5	1.42
75	5.4	1.22	5.4	1.13	5.3	1.22
100	5.3	1.14	5.3	1.04	5.3	0.91
125	5.3	0.61	5.2	0.52	5.2	0.41
150	5.2	Trace	5.2	Trace	5.2	Trace

Note: a =OD in EEL unit, b =g l^{-1}

Isolation of 3-Nitrotyrosine Resistant Mutant from Phenylalanine Auxotroph

Earlier experiments revealed that glucose and NH_4Cl were the best C and N sources and were optimum at 400 mM and 60mM levels, respectively. After optimization of the cultural condition of the single auxotrophs, the yields of L-tyrosine were 1.51 gm l^{-1} for P_{46}, 1.48 gm l^{-1} for P_{22}, and 1.49 gm l^{-1} for P_{79}. Thus, among the three auxotroph, P_{46} was found to be the best tyrosine producer. Further improvement of tyrosine yield of the mutant strain P_{46} was attempted by isolation of mutant resistant to 3-nitrotyrosine, the structural analogue of tyrosine. Prior to mutagenic treatment the sensitivity of 3-nitrotyrosine to auxotroph P_{46} was tested. The results indicate that MIC (minimum inhibitory concentration) of 3-nitrotyrosine for strain P_{46} was 5 mM. For isolation of analogue resistant mutant the strain P_{46} was treated with UV irradiation[16] and plated on an agar medium containing 10 mM of 3-nitrotyrosine. The isolated 12 nitrotyrosine resistant mutants were tested for tyrosine production under optimal condition. Tyrosine yield increased in comparison to the single auxotroph P_{46} (Table 8). The strain $P_{46}NT_E$ produces highest tyrosine (2.384 gm l^{-1}) among the selected 3-nitrotyrosine resistant strains. Similar increase in tyrosine production by analogue resistant strain of *Basillus subtilis*[23], *Corynebacterium glutamicum KY10233*[6], *Citrobacter freudii*[24], Brevibacterium lactofermentum[9] has been reported.

The present reporting of L-tyrosine production by phenylalanine auxotrophic 3-nitrotyrosine resistant mutant of *A. globiformis* seems to be the latest. Some further improvements in tyrosine yield by biochemical or genetic manipulation are being presently studied.

Table 8 — Tyrosine production by single auxotrophic analogue resistant mutant of *A. globiformis*

Mutant	Strain	
	Growth[a]	Tyrosine[b]
P_{46}	5.4	1.6
P_{46} NT_A	5.2	1.94
P_{46} NT_B	5.5	2.12
P_{46} NT_C	4.9	1.84
P_{46} NT_D	5.6	2.14
P_{46} NT_E	5.9	2.44
P_{46} NT_F	5.8	2.24
P_{46} NT_G	6.1	2.21
P_{46} NT_H	5.4	1.92
P_{46} NT_I	5.9	2.15
P_{46} NT_J	5.6	2.11
P_{46} NT_K	6.2	2.18
P_{46} NT_L	5.9	2.24

Note: a =OD in EEL unit, b =g l^{-1}.

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Strength and Reactivity of Corn Cobs Holocellulose Components

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Isolated hemicellulose from Egyptian corn cobs, as strength promoter and retention aid for Egyptian kaolin by bagasse pulp has been investigated. Addition of hemicellulose during paper making improves considerably the retention of kaolin by unbleached bagasse pulp. The influence of hemicellulose on the properties of filled paper is studied. Hemicellulose gives the best results as strength promoter and retention aid for kaolin fillers. The reactivity of the residual cellulose, after isolation of hemicellulose is studied and the reactivity of this residual cellulose with cotton linters and viscose wood pulp, toward xanthation is compared. It has been found that reactivity of residual cellulose corn cobs is higher than the other two cellulosic materials. Crystallinity index has been calculated from infrared spectra of the three cellulosic materials.

Introduction

Large quantities of corn cobs are accumulated annually in Egypt and hence it represents a potential source for cellulose and cellulose related industries. Removal of lignin from corn cobs leaves alpha cellulose and hemicellulose.

The term hemicellulose refers to mixtures of low molecular weight polysaccharides which are closely associated in plant tissues with cellulose.

Different methods have been developed for isolation of hemicellulose from plant materials [1,2]. Hemicellulose can be isolated from raw material by hydrolysis and extraction [3,4,5,6,7].

Holocellulose is prepared by acid chlorite [8,9,10] or chlorine dioxide oxidations [11,12] at elevated temperature.

Various studies have been reported for using the hemicellulose as a binder in paper making [13,14]. The plasticization, partial water solubility, and high surface area promoted by hemicellulose within fibres and on fibre surfaces result in increased fibre - fibre contact during paper formation and drying [15].

Hemicellulose can be also used to improve filler retention as well as paper strength [16].

In this paper, the influence of corn cobs hemicellulose as strength promoter for bagasse pulp and retention aid for Egyptian kaolin is reported.

Reactivity of cellulose remained after hemicellulose extraction compared with viscose wood pulp and cotton linters toward xanthation is also studied. Crystallinity index of the three cellulosic materials is also calculated from their infrared spectra.

Experimental

Raw Materials and Chemical Analysis

Egyptian corn cobs and Edfo-unbleached bagasse pulp were analyzed as follows :

(i) α-cellulose estimation according to Markblatt IV /29 Zellecheming (German Association of Cellulose Chemists and Engineers).

(ii) Pentosan was calculated according to Jayme and Sarten [17].

(iii) Lignin estimation was carried out according to the institute of Paper Chemistry Method [18].

(iv) Ash content was determined by ignition in muffle furnace at 400°C for 30 min. and then at 800°C for 45 min.

Table 1 — Influence of adding corn cobs hemicellulose on properties of paper

Added amount of hemicellulose (g hemi. / 100g pulp)	Retention value of hemicellulose, %	Breaking length, *m*	Tear factor	Burst factor	Brightness R_∞, %	Printing opacity $\frac{R_o}{R_\infty}$
None	—	1892	60	10.81	49	85.91
2	4.2	2558	25	13.49	44	91.49
4	7.5	2950	29	13.68	44	90.18
6	8.4	3488	32	13.94	44	89.02

Table 2 — Influence of kaolin addition on properties of paper sheets

Added amount of kaolin (g/100g pulp)	Retention value, %	Breaking length, *m*	Tear factor	Burst factor	Brightness R_∞ %	Printing opacity $\frac{R_o}{R_\infty}$ %
None	—	1892	60	10.81	49	85.91
5	3.44	1529	79	10.52	50	91.00
10	5.05	1431	77	10.36	51	92.07
15	8.27	1428	77	10.24	53	93.33
20	11.20	1426	74	9.09	54	93.45
25	28.27	1612	73	6.67	54	93.45

Different amounts of hemicellulose were added to the pulp during paper-making. The retention values of kaolin in the finished paper sheets are shown in Table 3.

From Tables 2 and 3 it is clear that the addition of hemicellulose to paper with kaolin, increases the retention of kaolin in the produced paper sheets. The retention of kaolin increases by increasing the amount of added hemicellulose. This can be due to the, addition of hemicellulose during paper sheet formation which increases the adhesive between the fiber and kaolin. Also presence of hemicellulose acts as a binder and increases the surface area which consequently increase the retention of the kaolin.

Table 3 — Retention of 15% kaolin (based on pulp) in preence of hemicellulose, rosin size and alum

Added amount of hemicellulose (g hemi/ 100g pulp)	2	4	6
Retention value of kaolin, %	60.99	77.77	96.93

Retention of Corn Cobs Hemicellulose by Bagasse Pulp in Presence of Kaolin

Retention of hemicellulose was determined in the prepared sheets as pentosans and the results are shown in Table 4.

The retention of hemicellulose was determined as the amount of pentosans retained in the finished paper sheet to the amount of hemicellulose originally added. (The difference between total pentosans in the finished paper sheet and pentosan content of the original pulp gives the amount of pentosans retained in the finished paper sheet).

It can be said that the presence of kaolin improves the retention of hemicellulose, due to the greater surface area of the clay particles which the hemicellulose coats. This leads to mutual improvement in the filler and hemicellulose retention.

Egyptian upgraded kaolin (Farch El-Ghozlan) which was prepared on pilot scale at CMRDI, El-Tebeen, Egypt was the paper filler used in this work with the following specifications:

Al_2O_3	35.21 %
Kaolinite	92.43 %
Total SiO_2	44.43 %
Fe_2O_3	00.92 %
TiO_2	1.38 %
Moisture content	00.73 %
Ash content	87.00 %
Brightness	73.90 %

Hemicellulose Isolation

Corn cobs were ground to 40-60 mesh and extracted with ethanol-benzene 1 : 1 for 6 hr. The holocellulose was prepared using the acetic acid-sodium chlorite treatment [1].

The hemicellulose was then obtained from holocellulose by extraction with 10% sodium hydroxide for 20 hr. at room temperature and liquor ratio 1 : 20. Then it was precipitated by acidification with 50% acetic acid to pH 4.5, followed by adding 3 volumes 95% ethanol. The hemicellulose was separated by decantation and solvent exchanged with 75% ethanol, 95% ethanol and ether, and dried under vacuum over calcium chloride.

Reactivity of Cellulose Material Toward Xanthation

Xanthation of residual cellulose of corn cobs, viscose wood pulp and cotton linters was carried out according to Fock method [19].

Degree of polymerization of cellulosic materials was carried out according to Jayme and Rasentock[20].

Infrared Spectra

Infrared spectra of the different cellulosic materials were obtained by using KBr disc technique using Apparatus JASCO FT / IR - 300 E. (Fourier Transform Infrared Spectrometer).

Results and Discussion

Unbleached bagasse pulp, delivered from Edfo paper Mill, Egypt and corn cobs are the raw materials used in this study and they have the following analysis.

Raw material	α-cellulose content,,%	Lignin (free ash) content, %	Pentosan content, %	Ash, %
Bagasse pulp	69.43	4.26	26.21	0.89
Corn cobs	43.20	25.50	30.99	2.00

Effect of Addition of Hemicellulose on the Mechanical Properties of Bagasse Paper Sheets

From Table 1, it is clear that addition of hemicellulose increases the mechanical properties of the paper sheets. This can be attributed to the increase in the adhesion force and crossing between fibers and consequently the inter-fiber bonding increase. These mechanical properties increase by increasing the added amount of hemicellulose. Unfortunately the tear and brightness of produced paper sheets decrease by increasing the amount of the added hemicellulose. This can be attributed to the addition of hemicellulose increase from the amount of hemicellulose of paper and consequently the crossing between the fibers increases causing a hardening of paper sheet fibers. This increase in hardening of paper sheet causes brittleness of the fiber.

Physical Properties of Paper Sheets Filled with Kaolin

Unbleached bagasse pulp was beaten to 30° SR before addition of kaolin. Different amounts of kaolin were added to the beaten pulp. The estimated retention values of kaolin in the prepared paper sheets are shown in Table 2.

From Table 2 it is clear that the retention of kaolin increases by increasing the added amount of kaolin. It is seen also from Table 2 that addition of kaolin in paper sheet formation decreases the mechanical properties of produced paper sheet. On the other hand, the brightness and printing opacity of the produced paper sheet after addition of kaolin increases [21]. This can be due to the increase of the high brightness and opacity of kaolin. These two values increase by increasing the added amount of kaolin.

Retention of Kaolin by Bagasse Pulp in Presence of Hemicellulose

The influence of the added hemicellulose on kaolin retention (15% kaolin) was studied.

Table 4 — Influence of adding corn cobs hemicelluilose on properties of filled paper

Added amount of hemicellulose (g hemi./100g pulp)	Retention value of hemicellulose, %	Breaking length, *m*	Tear factor	Burst factor	Brightness, R_∞ %	Printing opacity $\frac{R_o}{R_\infty}$ %
None*	—	1892	60	10.81	49	85.91
None**	—	1428	77	10.24	,53	93.33
2	10	,3302	42	17.63	52	93.30
4	12.5	3479	43	18.34	55	95.04
6	20	3926	45	21.76	58	96.37

*without kaolin and hemicellulose.
**without hemicellulose but with 15% kaolin solution

Influence of Corn Cobs Hemicellulose on Physical Properties of Filled Sized Paper Sheets

Properties of the prepared sheets from beaten bagasse pulp containing 2,4 and 6% hemicellulose (g hemi./100g pulp) and 15% kaolin (based on pulp) at a pH of 5-5.5 are displayed in Table 4.

From Table 2, it is clear that addition of kaolin during paper sheet without any retention aid causes a deterioration of the mechanical properties of paper sheet. This can be attributed to the decrease between fiber-fiber inter-bonding and consequently the crossing between fibers decreases. From Table 4 it is clear that addition of hemicellulose and kaolin causes an increase in the mechanical and physical properties of produced paper sheets. These mechanical properties increase by increasing the amount of hemicellulose added. This can be due to the increase of crossing and adhesion force between fibers of paper sheet.

Unfortunately, the tear strength of the produced paper sheet after addition of hemicellulose and kaolin decreases. This can be due to decrease in inter-fiber bonding between paper sheet fibers.

Infrared and Reactivity of the Different Cellulosic Materials

The infrared spectra of the different cellulosic materials are shown in Fig. 1. O'Conner and Co-workers[22] assigned the 7 m (1430 cm^{-1}) absorbance band to crystalline and 11 m (900 cm^{-1}) absorbance band to the amorphous form [23]. The crystallinity index (Cr.I) from the infrared spectra of different cellulosic materials is tabulated Table 5.

Table 5 — Crystallinity index (ratio of band intensity at 1430 cm^{-1}/band intensity at 900 cm^{-1}) and degree of polymerization of different celllulosic materials

Different cellulosic materials	Cr.I	D.P	wave number cm^{-1}
Cotton linters	1.85	1229	3429
Viscose wood pulp	1.45	934	3440
Residual cellulose of corn cobs	1.32	501	3446

From Table 5 it is clear that the crystallinity index of the corn cobs residual cellulose has the lower value than the other cellulosic materials.

The crystallinity index of the different cellulosic materials has the following sequence :

Corn cobs residual cellulose <viscose wood pulp <cotton linters.

This can also be confirmed from the shift of the -OH band at 3400 cm^{-1} to the left i.e., it is found in case of residual cellulose corn cobs at 3446 cm^{-1}, while it is at 3440 and 3419cm^{-1} in case of viscose wood pulp and cotton linters respectively (Table 5). This means that the residual cellulose has a lower hydrogen bond than the other two pulps due to the low wave number of the residual cellulose (3446). This can be attributed to the severe treatment of corn cobs to extract the significant hemicellulose[24]. These treatments have an effect not only on the crystallinity index but also on the degree of polymerization of the

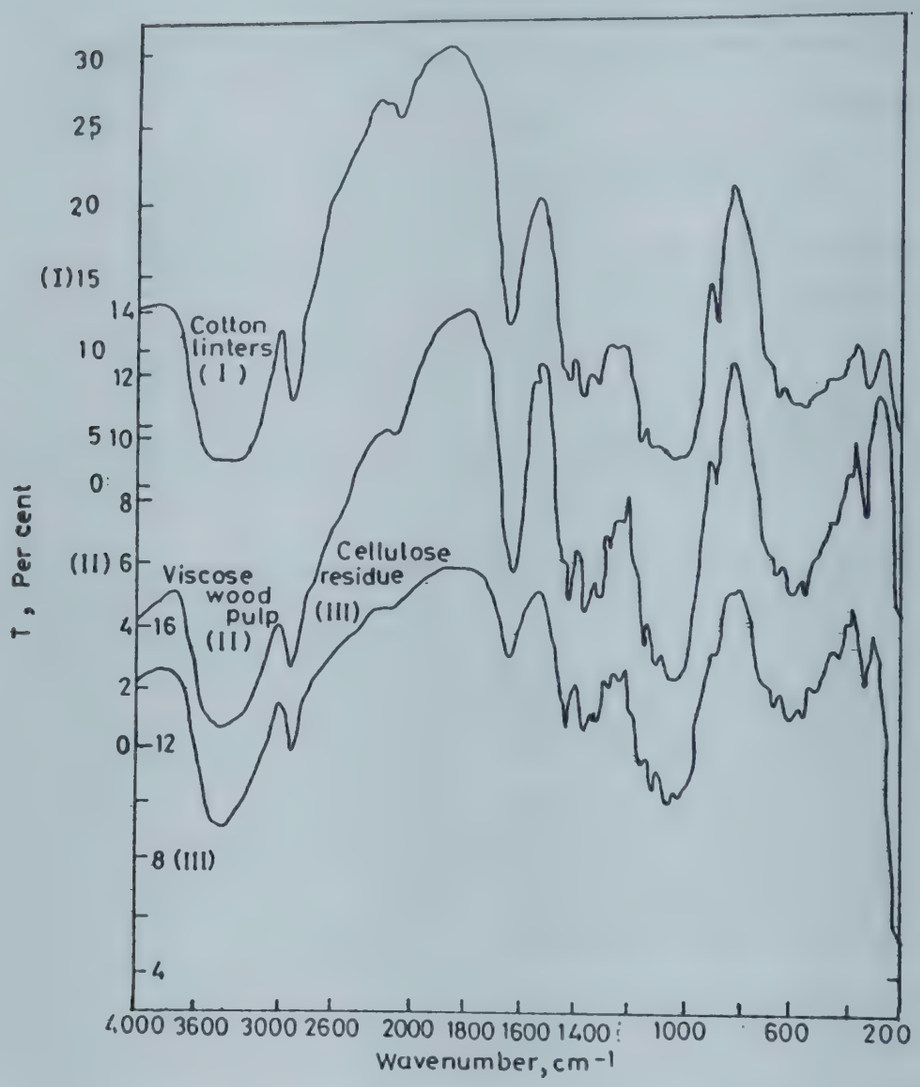

Fig.1 — Infrared spectra of different cellulosic materials

residual cellulose of corn cobs. So, from Table 5 it can be seen that the residual cellulose of corn cobs has the lower degree of polymerization than other cellulosic materials.

Reactivity of Cellulose Residue Remaining After Hemicellulose Extraction

High-cellulose residue (93% -cellulose) remained after extraction of corn cobs hemicellulose with 34.4% yield relative to raw material.

The analysis of this cellulose residue showed that it still contains 8.9% pentosans and insignificant amount of ash and lignin. Then reactivity of the prepared corn cobs cellulose towards xanthation was studied.

For the sake of comparison, a commercial viscose wood pulp and cotton linters samples were subjected to parallel experiments.

The selected cotton linters and wood pulp were more or less close to the corn cobs cellulose residue in chemical analysis. (Table 6).

The reactivity of different cellulosic materials toward xanthation shows that the corn cobs residual cellulose is more reactive than other cellulosic mate-

Table 6 — Analysis of cotton linters, viscose wood pulp and corn cobs cellulose residue

	Cotton linters	Viscose wood pulp	Cellulose residue of corn cobs
Alpha - cellulose, %	96.97	94.79	92.90
Pentosan, %	1.60	4.36	8.9
Ash, %	0.23	0.10	traces

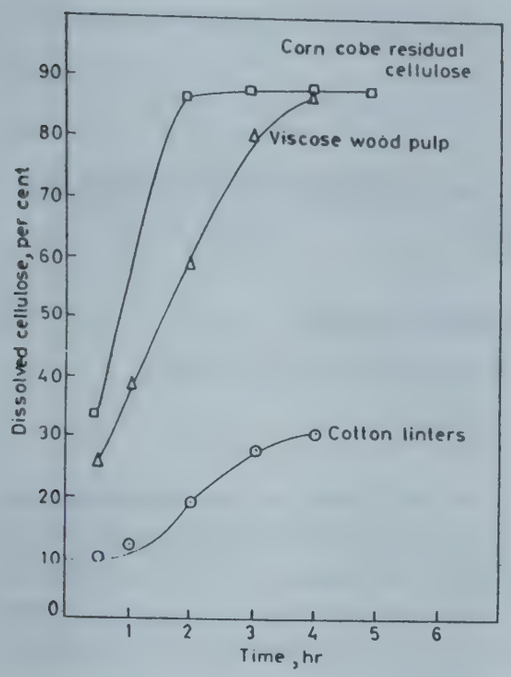

Fig.2 — Emulsion xanthation of different cellulosic materials, using CS_2 conventional method.

rials and has the following sequence as shown in Fig.2 :

Corn cobs residual cellulose >viscose wood pulp >cotton linters.

It thus finally can be concluded that the reactivity of cellulosic materials is highly affected not only on the crystallinity but also on the degree of polymerization of cellulosic materials.

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Filling of Blend Pulps and Improving the Retention of Filler by the Use of CMC

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Individual pulps from hard wood, rice straw, and bagasse have been beaten or their admixtures with addition of 10 per cent kaolin. The retention of the filler in the papers made from the blend was high. Effect of addition of carboxymethyl cellulose during the beating of pulps in the presence of filler has also been examined. The role of carboxymethyl cellulose is explained to be due to the chelation of the carboxymethyl cellulose with kaolin, and due to the improvement in the fiber-to-fiber bonding as a result of the increase of the hydrogen bonding.

Introduction

Mineral fillers have long been used in paper making. Earlier, they were used to obtain a more closed surface for writing papers and to improve the writing properties. Today, the main reason for the use of fillers in printing paper is to increase printability. They not only produce more smoothness and a gloss after calendering but also more brightness and opacity.

Filler must be well anchored to the fiber so that it will not dust out during calendering or printing of the paper. Kaolin, an aluminium silicate, is the most frequently used filler[1].

Mahanta[2] proved that molecular weight is important in filler retention and drainage aids. Lorz[3] showed that the decrease of the air content and improvements in retention and drainage are important in achieving the best quality of paper for each specific application.

Addition of carboxymethyl cellulose CMC at the size press improves the grease resistance, decrease the porosity, and improves the strength properties of paper[4].

Barper[4] has also shown that how a molecular configuration similar to cellulose fiber and water solubility contributed by the hydrophilic carboxymethyl (CH2-COO Na) groups ought to make CMC a very effective dry-strength additive, which is actually not so. Tests with radioactive CMC showed that normal CMC was unevently retained. Another deteriment is that aluminium ions lowered strength by a gellation of CMC. These drawbacks were overcome by a reduction in the degree of substitution of a special cellulose to a figure of 0.4.

In a previous work(5), it has been concluded that the physical, optical and mechanical properties of paper depend more or less on the type of pulp used. They found that the decrease or increase of the retention of fillers into papers depends on the type of pulps and fillers. Therefore, experiments were carried out on a blend of three pulps, namely hardwood pulp, bagasse pulp, and rice straw pulp. Blending was carried out in the Valley beater and filled papers from each pulp were also prepared. Addition of 10 per cent kaolin was made after the start of the beating within specific duration depending on the type of pulp to obtain better filler's retention per centage. Improving the retention of filler is done by adding carboxymethyl cellulose (CMC). The role of CMC in retaining filler has been explained.

Materials and Methods

In this study, bleached hardwood pulp, bagasse and rice straw pulps delivered from Rakta Co. for Pulp and Paper, Alexandria, Egypt were analyzed for α-cellulose, hemicellulose, and ash content accord-

ing to the Germany Standards Merkbldt (III) and the results are given in Table 1.

Table 1 — Analysis of pulps

Type of pulp	α-Cellulose, per cent	Hemicellulose, per cent	Lignin, per cent	Ash, per cent
Hardwood pulp	87.6	8.24	0.56	1.1
Bagasse pulp	72.9	24.9	1.5	1.3
Rice straw pulp	68.4	23.5	5.3	1.6

Preparation of Hand-made Paper Sheets

Paper sheets were prepared according to TAPPI standard methods using the sheet former of AB Lorentzen and Wetter (Stockholm, Sweden). A sheet of 165 mm in diam and 214 cm2 surface area was formed using 1.43 g oven-dry pulp. The sheets were conditioned between 18 and 20 °C and at relative humidity of 65 per cent.

The conditional paper sheets were weighed and the thickness of each sheet was measured. The physical and mechanical properties of the formed sheets were investigated.

Results and Discussion

Filled Paper From Blended Pulps

The properties of filled paper from each of the individual pulp were studied. From Table 2, it is evident that wood pulp was beaten for 50 min in the

Table 2 — Pulps at constant S° R 50

Experiment	Time of beating min	Density, g/cm	Brightness, per cent	Test Tappi Opacity, per cent	Tear, g	Burst, Kgm/cm^2	Breaking length, m	Retention, per cent
Wood paper pulp	50	0.5	76.6	92	86	1.98	3035	0
Wood paper pulp +10 per cent kaolin	40	0.5	75	90	70	1.81	3210	20
Bagasse paper pulp	15	0.4	69	90.4	72	1.96	2917	0
Bagasse paper pulp +10 per cent kaolin	14	0.4	65	94	68	1.80	3380	24
Rice straw paper pulp	8	0.34	74.5	96.5	40	0.60	1375	0
Rice straw paper pulp + 10 per cent kaolin	8	0.3	70	98.2	44	0.50	850	43
Mixture	12	0.35	76.5	96.5	72	0.86	1630.5	0
Mixture +10 per cent kaolin	12	0.37	74.4	96.5	74	1.40	1795	51
Wood pulp +10 per cent kaolin +2.5 per cent CMC	25	0.5	81	90	105	2.00	3130	25
Bagasse pulp +10 per cent kaolin +2.5 per cent CMC	12	0.4	68.5	92.6	68	1.80	3000	29.5
Rice straw pulp +10 per cent kaolin +2.5 per cent CMC	8	0.3	76.5	97.2	44	0.65	1275	52
Mixture +10 per cent kaolin +2.5 per cent CMC	10	0.4	73.4	95.6	74	1.00	1650	57

— The mixture consisted of 10per cent wood paper pulp, 20 per cent bagasse paper pulp and 70 per cent rice straw paper pulp; CMC — carboxymethyl cellulose.

Valley beater to reach freeness (50 S° R). On addition of 10 per cent kaolin based on the pulp as filler after the start of beating within 10 min, the time of beating to reach 50 S° R decreased to 40 min. The optical properties for the filled and unfilled paper namely brightness and opacity were practically same Table 2. The burst strength and the tear resistance slightly decreased for filled paper while the breaking length increased.

On working with bagasse pulp the time of beating to reach S° R 50 was 15 min. On adding 10 per cent kaolin after the start of beating within 30 min the time of beating decreased to 14 min . The brightness per cent of the filled paper was lower than that of unfilled paper, i.e., 75 and 69, respectively, while the opacity slightly increased. The tear resistance and the burst strength decreased for filled papers while the breaking length increased (Table 2).

For rice straw pulp, the time of beating of pulp to reach S° R 50 did not change after the addition of 10 per cent kaolin and the start of beating within 2 min. The brightness was low, i.e. 40 and 44 per cent for the unfilled and filled papers, respectively, while the opacity of the latter increased than the former (Table 2). Also, the tear resistance slightly increased, while the breaking length and the burst strength decreased.

It is evident from the retention values of filler into paper made of these three pulps that the more value was for rice straw pulp. The per cent was 43, which means that 43 per cent of added filler remained in the paper, followed by wood pulp and then bagasse pulp which reached 25 per cent and 24 per cent, respectively. Also, it is evident from the results of these experiments that the densities of the filled and unfilled paper were practically the same. Also, the values of the density decreased in the order : Wood pulp >bagasse pulp >rice straw pulp.

From the results in Table 1, it is evident that the chemical properties of the pulp have a certain effect on the properties of the papers prepared therefrom. For rice straw pulp, the lignin content reached 5.3 per cent (Table 1) compared with that for bagasse pulp (1.5 per cent) and for the wood pulp [0.56 per cent Table 1]. It is evident that the presence of the lignin influence both the brightness which is low for rice straw than both bagasse and wood pulp. Also the opacity of paper made from rice straw pulps is higher than those made from bagasse and wood pulp. Lignin with its network structure lead to low bursting and breaking length of papers made from wood and bagasse pulps (Table 1 and 2). The presence of lignin decreased bonding between the fibers in rice straw pulp and the filler added, which leads to decreased bursting and breaking length of the papers prepared from rice straw pulp on comparison with the pulps containing low lignin per cent; wood pulp. The retention value of the filler added to rice straw pulp is high compared with that added to bagasse or wood pulps. Again the network structure of lignin in pulp helped to retain the filler granules, and increased the retention values (Table 1 and 2).

Mixture of these three pulps of 10 per cent wood pulp, 20 per cent bagasse pulp and 70 per cent rice straw pulp (since the second and the third pulp are the main pulps produced in Egypt), were beaten in the Valley beater (Table 2), to reach S° R 50. The time of beating of the mixture to reach 50 was lower than the time required for beating wood and bagasse pulps but higher than that of rice straw pulp. The density of the paper prepared from the mixture was practically similar to each pulp. The brightness and the opacity of these papers were slightly higher than both papers prepared from bagasse or rice straw pulp and the brightness was lower than the papers prepared from wood pulp. the strength properties of the papers prepared from the blend pulps were lower or practically the same with the papers prepared from either bagasse or wood pulp while they were higher than the papers prepared from rice straw pulp. Thus blending of 10 per cent wood pulp and 20 per cent of bagasse pulp with 70 per cent rice straw pulps increased the properties of the papers compared to those papers prepared from rice straw pulp only.

Addition of 10 per cent kaolin to this mixture after the start of beating with 3 min (based on the per centages of the different pulps) the time of beating to reach S° R 50 did not change. The density and the opacity were practically the same for the filled and unfilled papers (Table 2). It is also evident from Table 2, that the bursting strength and the breaking length slightly increase on adding the filler to the pulp in the Valley beater. Also the tear resistance slightly increased.

The retention of filler into papers made from mixed pulps significantly increased to 51 per cent compared with the other values of the other papers (Table 2).

Conclusions

Carrying out the filling process for blending pulp in Valley beater improved the retention of fillers, meanwhile the brightness and opacity of the blended filled papers were practically the same or slightly higher than the filled papers of each pulp. On the other hand, the mechanical properties, namely the breaking length and bursting strength of the filled papers from blended pulps were lower than those of filled papers from each pulp, namely wood pulp, bagasse pulp or rice straw pulp, respectively (Table 2). The tear resistance of filled papers from mixed pulps was higher than the tear resistance of papers made from rice straw pulp, wood pulp or bagasse pulp individually (Table 2). Thus, the presence of the three pulps in mixture leads to filled papers of improved properties compared with the filled papers prepared from rice straw pulp.

Addition of Carboxymethyl Cellulose Retention Aids.

The presence of the hemicellulose decreased the beating time due to its hygroscopicity which facilitates the fibrillation of the beated pulps, therefore carboxymethyl cellulose was used to achieve the same function because of its high hygroscopicity. Wood pulp, bagasse pulp, or rice straw pulp were beated in the valley beater to which two per cent kaolin was added together with 25 per cent carboxymethyl cellulose, D.S 1.0 after the start of beating withen the time mentioned for the filling of papers without CMC (Table 2). On comparison the beating time required to reach 50 S° R in the presence of 10 per cent kaolin with that time required in the presence of both kaolin and 2.5 per cent CMC (Table 2), it is evident that the time decreased form 40 to 25 min, respectively. On the other hand, the prightness and tear resistance were significantly increased while the breaking length slightly decreased. Addition of CMC also increased the retention of filler. For bagasse pulp the addition of 2.5 per cent CMC together with the filler increased the retention of the filler from 24 per cent to 29 per cent. The same results were obtained when CMC was added to the rice straw pulp together with the filler (Table 2), where the retention of filler increased significantly from 43 to 52. The brightness and the breaking length of the paper sheets increased, while the opacity, tear resistance and bursting strength were practically the same. Finally, addition of CMC as adhesive to the wet web of the blended pulps in the beater after the start of beating together with the filler, allowing the time of beating to reach 50 S° R decreased frm 12 to 10 min and the retention of filler increased from 51 to 57 per cent (Table 2). On the other hand, the breaking length and the bursting strength decreased. The optical properties, namely brightness and opacity were practically the same. The densities of the filled papers either in the presence or in the absence of CMC did not change (Table 2).

Various investigators[6-9] have found that the chemical and physicochemical properties which are important for the adsorption of polymer molecules by clay colloid, include the nature of the functional groups in the molecule; and its shape, molecular weight conformation and polarity. These properties, in turn, determine the polymer abilities to bind by hydrogen bonding or by ionic, covalent or chelate structures[6-9]. Owing to these findings, the presence of carboxymethyl cellulose which is a polyelectrolyte together with kaolin may bind together through chelation, hence they are retained into fiber as a result of the increase of the fiber-to-filler bonding arising from the presence of CMC inbetween the fibers and the filler. On the other hand, due to the presence of carboxylic and hydroxyl groups in the carboxymethyl cellulose, more hydrogen bonding may be formed which permits the approach of the improvement of the fiber-to- fiber bonding, consequently the retention of the fillers into fibers increased as well as the strength properties of the papers also increased.

Concluding Remarks

- In Valley beater the time of beating to reach the degree of freeness equivalent to 50 S° R decreased on adding 10 per cent filler after the start of beating.
- Adding filler did not affect the physical and optical properties. However the mechanical properties slightly decreased.

- The high filler retention per cent was achieved for papers made from rice straw pulp followed by wood pulp and then bagasse pulp. the presence of high lignin in rice straw pulp increased the retention of filler.
- The time of beating of blend of wood pulp 10 per cent, bagasse pulp 20 per cent and rice straw pulp 70 per cent decreased to 12 mins. Addition of filler to the blend had no effect on the time of beating.
- The densities of the filled and the unfilled papers made from the blend pulps were practically the same.
- The retention per cent of fillers into papers made from blend pulp was higher than those of the individual pulp.
- Addition of CMC to the pulps increased the retention of the filler as the CMC could chelate with the filler and increased the fiber-to filler bond. The presence of hydroxyl and carboxyl groups in the CMC increased the number of hydrogen bonds and hence the fiber-to fiber bonds, thus, the strength properties of the papers consequently improved.

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Uptake of Lead by Iron Oxyhydroxides

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The paper presents investigations on the adsorption of lead on hydrated iron oxides prepared at different temperatures from solutions of iron(II) sulphate or chloride using alkalis such as sodium hydroxide, sodium carbonate and calcium hydroxide followed by aerial oxidation, filration and drying. A comparative study has been made on the fresh and the aged samples of these iron oxides. It is observed that almost all the samples are good adsorbents of lead but the one prepared from iron(II) chloride – sodium carbonate system is the best under the studied conditions.

Introduction

Iron(III) oxides form an important class of commercial materials owing to their application as pigments, catalysts and absorbers of gases and ions[1]. The hydrated iron(III) oxides are used for adsorption of poisonous gases from chimneys of industries and heavy metals from effluents and drinking water[2]. They can also be used to extract valuable metals present at trace levels in sea water.

Lead has been closely associated with human civilization since centuries. It is an essential commodity in the modern industrial world ranking fifth in consumption after iron, copper, aluminium and zinc[3]. But, lead and its compounds are cumulative poisons. It enters the sources of water from a number of industrial and mining effluents, automotive exhaust, leaded gasoline, storage batteries, printing and pigment industries, zinc mines and smelters.

The capacity of hydrous iron oxides to remove potentially toxic heavy metals including lead is well-documented[4]. Methods have been developed in the laboratory to prepare hydrated iron(III) oxides by aerial oxidation of iron(II) hydroxides obtained by the addition of an alkali to an iron(II) salt solution[5]. The present paper examines the adsorption capacity of these samples for lead ions in solution.

Experimental

The reagents used in the investigation were of analytical grade. Chloride or sulphate of iron(II) was used as source of iron while sodium hydroxide, sodium carbonate or calcium hydroxide were the alkalis employed. Iron(II) chloride was prepared from iron powder and HCl under carbon dioxide atmosphere.

Preparation of Sorbents

200 mL of iron(II) solution (containing 11g iron) was taken in a reaction vessel and 10% solution of the alkali was added with constant stirring till neutralisation. Some more alkali was added so that it was in slight excess of stoichiometric requirement. Air was bubbled through the reaction mixture at the rate of 2-3 L/min for about 8-h. The precipitate was filtered, washed with 2% ammonium nitrate followed by distilled water and dried in an air oven at 110°±5°C. The reaction was carried out at four different temperatures, i.e. 30°, 50°, 65° and 80°C.

Characterization of Sorbents

Surface area of the sorbents was measured using a 'Micromeritics High Speed Surface Area Analyzer' employing the BET technique. Particle size distribution of the samples was investigated on a 'Micromeritics Sedigraph'. XRD of the samples was studied on a Phillips Diffractometer.

Sorption Procedure

The solution of lead nitrate was prepared in 0.2*N* sodium nitrate solution to contain about 20 ppm of lead. 100 mL of this solution were taken in a polythene bottle and its *p*H was adjusted to 5, using dil.NaOH or HCl. After introducing 200 mg sorbent, the bottle was stoppered and kept for 20h with intermittent agitation. The solid was then separated by filtration and the filtrate was analyzed for its lead content by atomic absorption spectrophotometry. Lead adsorbed on the sorbent was found by difference. Fresh as well as samples aged for one year were used as sorbents. The results are presented in Tables 1-5.

Results and Discussion

Effect of Anions

Ferrous sulphate is a commonly available and less expensive starting material for the preparation of iron compounds[6]. However, in the case of hydroxides, sulphate accompanies through adsorption and affects the surface characteristics of the sample[7]. For this reason, ferrous chloride was chosen as the starting material. Results (Tables 1-5) indicate that, in general, all the samples are good adsorbents of lead, but samples prepared from chloride showed better adsorption and resistance to ageing (Tables 3, 4 & 5) compared to those from sulphate (Tables 1 & 2) under similar conditions. There are also a few excep-

Table 1 — Adsorption of lead by hydrated iron oxides prepared from the system $FeSO_4$+NaOH

Preparation temperature (°C)	Phases present	Surface area (sqm/g)	Average particle size (μm)	Adsorption by fresh sample (%)	Adsorption by one year aged sample (%)
30	Fe_3O_4 & γ-Fe_2O_3	25.53	21.69	42	41
50	Fe_3O_4 & γ-Fe_2O_3	19.05	20.70	69	65
65	Fe_3O_4 & γ-Fe_2O_3	12.42	20.95	68	34
80	Fe_3O_4 & γ-Fe_2O_3	8.71	21.52	51	45

Table 2 — Adsorption of lead by hydrated iron oxides prepared from the system $FeSO_4$ +Na_2CO_3

Preparation temperature (°C)	Phases present	Surface area (sqm/g)	Average particle size (μm)	Adsorption by fresh sample (%)	Adsorption by one year aged sample (%)
30	α-FeOOH &ε-Fe_2O_3	46.5	18.34	92	90
50	α-FeOOH &ε-Fe_2O_3	23.99	10.44	93	92
65	α-FeOOH, ε-Fe_2O_3 & γ-Fe_2O_3	19.06	10.44	65	49
80	α-FeOOH, ε-Fe_2O_3 & γ-Fe_2O_3	7.83	23.94	62	54

Table 3 — Adsorption of lead by hydrated iron oxides prepared from the system $FeCl_2$ +NaOH

Preparation temperature (°C)	Phases present	Surface area (sqm/g)	Average particle size (μm)	Adsorption by fresh sample (%)	Adsorption by one year aged sample (%)
30	γ-FeO_3 & ε-Fe_2O_3	17.47	15.88	27.68	25
50	γ-FeO_3 & Fe_3O_4	11.71	21.00	66.12	55.37
65	γ-FeO_3 & Fe_3O_4	8.45	17.62	70.43	68.81
80	γ-FeO_3 & Fe_3O_4	6.22	24.18	100.00	99.46

Table 4 — Adsorption of lead by hydrated iron oxides prepared from the system $FeCl_2$ +Na_2CO_3

Preparation temperature (°C)	Phases present	Surface area (sqm/g)	Average particle size (μm)	Adsorption by fresh sample (%)	Adsorption by one year aged sample (%)
30	α-FeOOH & ε-Fe_2O_3	45.32	15.16	88	82
50	α-FeOOH & ε-Fe_2O_3	21.10	20.21	100	96
65	α-FeOOH & α-Fe_2O_3	62.50	12.95	95	90
80	α-FeOOH & α-Fe_2O_3	6.38	20.16	95	91

Table 5 — Adsorption of lead by hydrated iron oxides prepared from the system $FeCl_2$ +$Ca(OH)_2$

Preparation temperature (°C)	Phases present	Surface area (sqm/g)	Average particle size (μm)	Adsorption by fresh sample (%)	Adsorption by one year aged sample (%)
30	γ-Fe_2O_3 & ε-Fe_2O_3	125.98	18.88	100	99
50	γ-Fe_2O_3 & ε-Fe_2O_3	36.43	17.66	100	96
65	γ-Fe_2O_3 & Fe_3O_4	23.83	22.15	58	54
80	γ-Fe_2O_3 & Fe_3O_4	8.20	24.74	62	61

tions indicating the importance of other factors such as phase composition.

Effect of Phases and Alkali

In general, Na_2CO_3 addition resulted in samples with higher adsorption, be it in sulphate or chloride media. This may be ascribed to the phase composition of the resultant precipitates. The presence of γ-Fe_2O_3 seems to affect adsorption (Table 1), but results from $FeCl_2$-$Ca(OH)_2$ system (Table 5) do not support this theory. Here adsorption decreased with the disappearance of ε-Fe_2O_3 . On the contrary, in the $FeCl_2$-NaOH system (Table 3), adsorption increased after the ε-Fe_2O_3 disappeared, indicating the significance of phase composition also in affecting adsorption. Nevertheless, α-FeOOH, α-Fe_2O_3 and ε- Fe_2O_3 in combination seem to be contributing to the higher adsorption of lead (Tables 2-4). However, detailed study on the percent composition of the phases of iron oxyhydroxides is required for any valid conclusion.

Effect of Preparation Temperature

Results in Tables 1-4 show that, in general, all the samples have reasonably good adsorption which reaches a maximum for those prepared at 50°C and then decreases for the ones at 65° and 80°C. This may be due to partial neutralisation of the hydroxyl group residing at the surface of the hydrous iron oxides at preparation temperatures beyond 50°C. The importance of the surface hydroxyl groups for ion adsorption through surface complexation has been discussed by Stumm *et al.*[8]. As mentioned earlier, variation in the phase composition with temperature could be another factor. The trend is reversed in the case of $FeCl_2$-NaOH system (Table 3) where the adsorption progressively increased with temperature probably due to the formation of relevant phase composition. In the case of $FeSO_4$-NaOH system (Table 1), this trend might have been disturbed due to varying quantities of adsorbent sulphate on the samples prepared at different temperatures. The system $FeCl_2$-$Ca(OH)_2$ (Table 5) is interesting in that a sample with 100% adsorption could be obtained at room temperature (30°C), the sample retaining its

efficiency even after ageing. The efficiency of $Ca(OH)_2$ for sulphate system was not studied obviously due to the co-precipitation of $CaSO_4$.

Effect of Surface Area and Particle Size

Data presented in Tables 1-5 clearly indicate that there is no systematic increase or decrease in the adsorption with enlargement of surface area or variation in particle size. Possibly, lead adsorption takes place on the active surface sites of the hydrous iron oxides through interaction of the surface hydroxyl with $PbNO_3$ $^+$species[9].

Conclusions

1) Hydrated iron oxides prepared from iron(II) chloride system exhibit better adsorbent properties.

2) Sodium carbonate as a precipitant results in samples with better adsorption capacity.

3) α-FeOOH, α-Fe_2O_3 and ε-Fe_2O_3 in combination show excellent adsorption capacity for lead.

4) Hundred percent adsorption of lead, in the studied range, is obtained for $FeCl_2$-NaOH system at 80°C, $FeCl_2$-Na_2CO_3 system at 50°C and $FeCl_2$ + $Ca(OH)_2$ system at 30°C and 50°C.

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Adsorption Dynamics of Hemoglobin at the Activated Carbon Fiber Solution Interface

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The kinetic behaviour of the adsorption of hemoglobin onto the activated carbon fiber (ACF) surfaces is studied from the alkaline solution of the protein at room temperature. Various adsorption and kinetic parameters such as the adsorption coefficient (K), rate constants for the adsorption and desorption (k_1 and k_2), diffusion constants (D) and penetration rate constants (k_p) are calculated under varying experimental conditions. The effects of addition of inorganic salts, surface active agents (CTAB and sodium oleate) and aliphatic alcohols are investigated on the adsorption of hemoglobin. The effect of temperature on the adsorption is also studied and various thermodynamic parameters are evaluated.

Introduction

The phenomenon of protein-surface interaction is significant in many biological and industrial processes such as protein purification, selection of dialysis membranes, cell immobilization, drug delivery systems, and design of biocompatible materials for surgical implants[1-4]. Apart from these applications the phenomenon is of fundamental importance in chromatographic separation techniques. Thus, considering various applications of protein adsorption, the present investigation is undertaken to study the dynamics of the adsorption of hemoglobin onto the activated carbon fiber (ACF) surfaces.

Experimental Procedure

Materials and Methods

The hemoglobin powder, used as an adsorbate, was supplied by the Loba Chemie (India). The molecular weight and isoelectric point of the protein were reported as 67,000 and 6.8 respectively. The activated carbon fibers were provided by the National Physical Laboratory, New Delhi, India having a specific surface area of 1500 m^2g^{-1} with pore sizes < 20 nm. Throughout the experiment bi-distilled water was used and other chemicals required were also of AR grade.

The method of adsorption was similar to that described earlier[5-8]. In a pyrex flask 25 ml of an alkaline solution (pH 12.7) of hemoglobin containing 0.2 g of well crushed ACF was taken. The suspension was agitated constantly for 2h by a mechanical stirrer (Toshniwal,India). After the shaking was over, the suspensions were centrifuged and the supernatants analyzed for the remaining hemoglobin by a direct colorimetric method[9]. The adsorbed hemoglobin (mg g^{-1}) was calculated using Eq.(1).

$$q = \frac{(C_o - C_e)\,V}{m} \qquad ...(1)$$

where, q = Amount of adsorbed hemoglobin (in mg g^{-1}), C_o = Initial concentration of hemoglobin solution, C_e = Equilibrium concentration of hemoglobin solution, V = volume of the suspension (ml), and m = Amount of the adsorbent (g).

Kinetics of Adsorption

To study the kinetics of adsorption the progress of the adsorption process was monitored by determining the amounts of adsorbed hemoglobin at various time intervals.

Results and Discussion

Adsorption Isotherm

When the concentration of hemoglobin solution is increased in the range 0.44 to 5.18 × 10^{-5} mol dm^{-3} the amount of adsorbed hemoglobin increases and finally attains a saturation value (plateau value) as reported earlier[11,12]. The adsorption isotherm in the present case is shown in Fig.1 in which the greater slope indicates a high affinity for adsorption. The isotherm is indicative of the Langmuir type of adsorption and belongs to L2 category of adsorption isotherm[13].

The numerical value of the adsorption coefficient ($K = k_1/k_2$) was calculated from the linearized Langmuir adsorption isotherm, shown in Eq.(2) :

$$\frac{C_e}{q} = \frac{1}{K_1 K} + \frac{C_e}{K_1}, \qquad ...(2)$$

and was found to be 3.3 × 10^4 dm^3 mol^{-1}.

Such a high value of adsorption coefficient also implies a greater affinity of hemoglobin for adsorption.

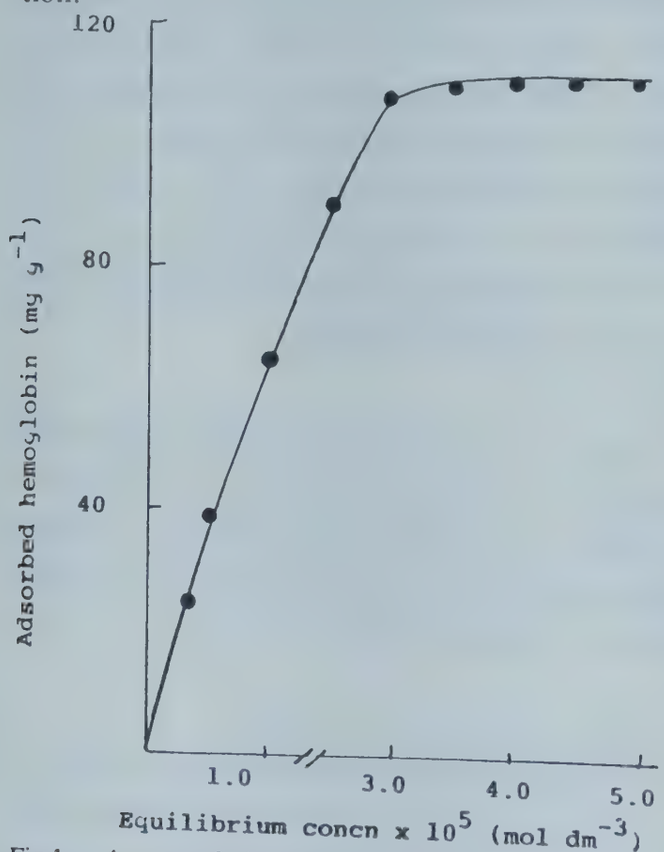

Fig.1 — Amount of adsorbed hemoglobin (mg g^{-1}) vs the equilibrium concentration

Kinetics of Adsorption

The kinetics of the adsorption of protein molecules is interesting, as it involves the following rate controlling steps[14] :

(i) Transport of protein molecules towards the surface by diffusion and/or convection,

(ii) Attachment of protein molecules at the active sites on the surface, and

(iii) Changes in the confirmation of the adsorbing protein molecules.

Thus, for studying the mechanisms of the kinetics of the adsorption process the progress of the adsorption was monitored, as shown in Fig.2. It is evident from Fig.2 that the rate of adsorption is almost constant up to 75 min and then it gradually decreases with time. Actually, the adsorption kinetics of end-functionalized large chains is a two regime process[15-17]. At the initial stages, the substrate surface is bare and the kinetics of adsorption is governed by the diffusion of the chains from the bulk solution to the surface. All the chains that arrive at the interface are considered to be immediately adsorbed. The mass transport can be interpreted as a Fickian diffusion. The diffusion coefficient D is obtained from the slope of the curve q as a function of t which depends on the bulk concentration C_o

$$q = \frac{2}{\sqrt{\pi}} C_o \sqrt{Dt}. \qquad ...(3)$$

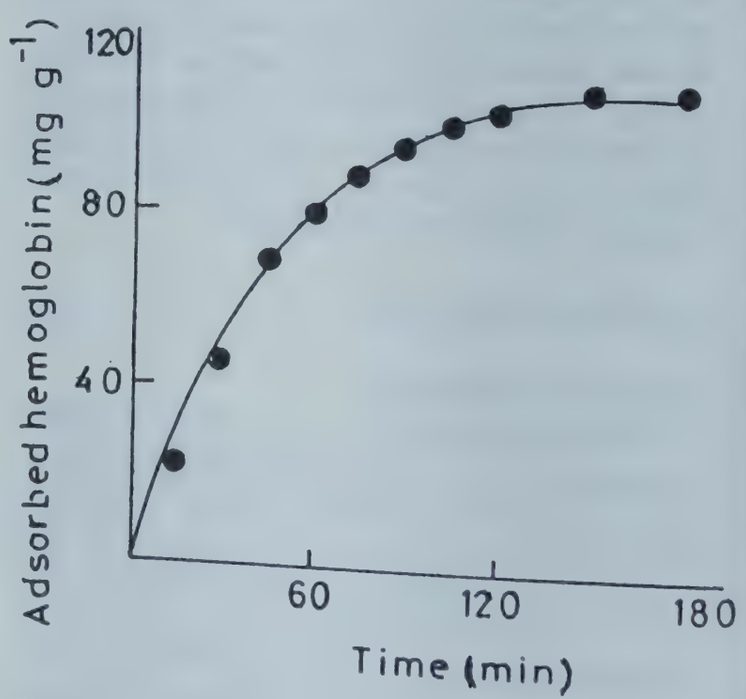

Fig.2 — Amount of hemoglobin adsorbed (mg g^{-1}) vs time for fixed [hemoglobin] = 2.98 × 10^{-5} mol dm^{-3}, [ACF] = 0.2 g, pH = 12.7, temperature = 25 ± 0.2° C

From the slope of the curve q as a function of $\sqrt{t}$ shown in Fig.3, for the hemoglobin solution at the bulk concentration 2.98×10^{-5} mol dm^{-3}, the diffusion constant is determined as 1.0×10^{-8} cm^2 s^{-1}.

We have also calculated the diffusion constants for varying hemoglobin solutions and results are summarized in Table 1. It is revealed from Table 1 that with increasing bulk concentration of hemoglobin solution the diffusion constants also increase.

After the initial step, an activation barrier of adsorbed chains is formed which governs the kinetics because the chains arriving from solution have to diffuse across the barrier. Ligowe and Leibler[15] considered a simplified model where the adsorbed amount (or the surface coverage) approaches exponentially an equilibrium adsorbed amount q_e with time, introducing a characteristic penetration time T.

$$q = q_e [1 - \exp(-t/T)] . \quad ...(4)$$

Equation (4) indicates that the second process has an exponential nature, and the penetration rate may be obtained from the slope of $[\ln(q_e - q)]$ as a function of time. The exponential behaviour shown by hemoglobin solution of varying bulk concentrations is, as shown in Fig.4. From the slope of the straight line for longer durations in Fig.4, the penetration rate constant k_p ($= 1/T$) have been calculated and are given in Table 1.

We have also evaluated the rate constants for adsorption (k_1) and desorption (k_2) from Eq.(5)[18-19]

$$\frac{1}{C} = k_1 t + \frac{1}{C_o} . \quad ...(5)$$

Salt Effect

The addition of low molecular weight electrolytes to adsorption systems has significant effect on the adsorption kinetics[20,21]. The presence of ions in protein solution influences the charge- profiles of the protein molecules in multiple ways. The situation can be understood more realistically by assuming that if a large charge is fixed in a solution of simple salt, the effect of the coulomb potential from the charge is

Table 1 — Various kinetic parameters of the adsorption process for varying hemoglobin concentrations

Initial hemoglobin concentration	Penetration rate constant	Diffusion constant	Rate constant for adsorption	Rate constant for desorption
$C_o \times 10^5$ mol dm^{-3}	$k_p \times 10^3$ min^{-1}	$D \times 10^8$ cm^2 s^{-1}	$k_1 \times 10^4$ s^{-1}	$k_2 \times 10^8$ mol dm s^{-1}
1.49	1.1	0.58	7.2	2.1
2.24	0.76	6.81	9.4	2.8
2.98	0.63	1.0	13.2	4.0

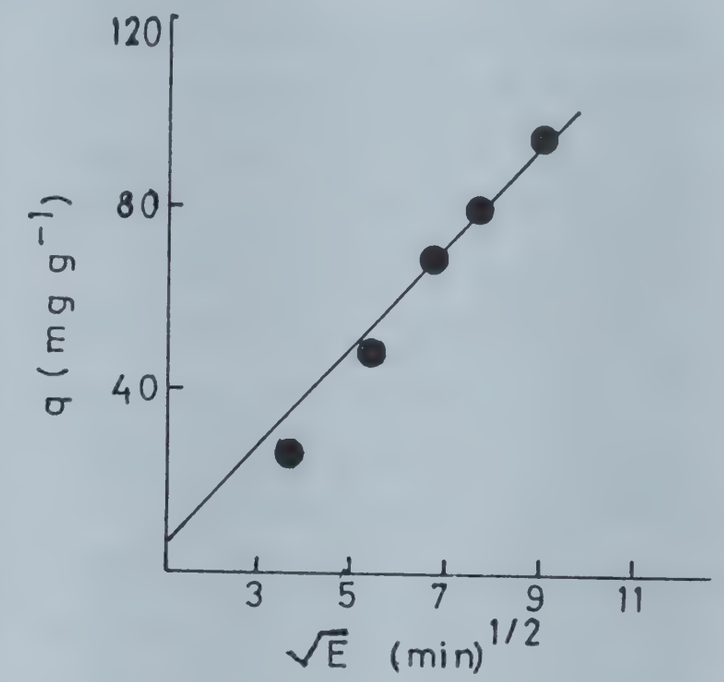

Fig.3 — Adsorbed amount (q) as function of $\sqrt{t}$

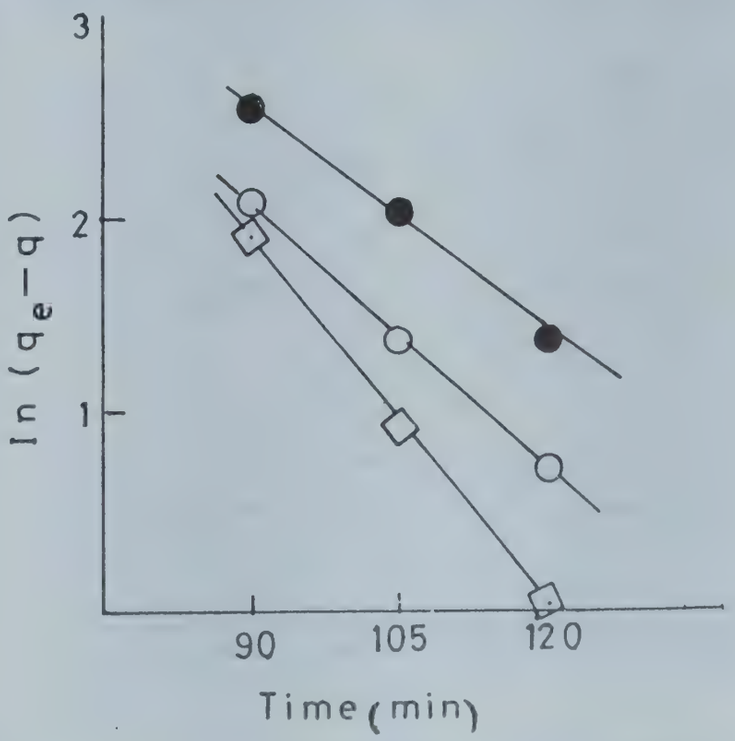

Fig.4 — A plot showing the variation of ln (q_e - q) with longer durations (t) at varying hemoglobin concentrations, (✕) 2.98, (□) 2.24, and (+) 1.49×10^{-5} mol dm^{-3}

screened by the ionic atmosphere due to the presence of small ions. This screening becomes more effective with an increase in the salt concentration. It has been shown earlier that in a poly-electrolyte solution, the quality of solvent decreases in the presence of salts and, therefore, the adsorption should also increase[22].

In the present study the effect of the addition of salts on the amount and rate of the adsorption has been studied by adding different electrolytes in the concentration range 0.5 to 3.0×10^{-2} mol dm^{-3}. The results shown in Fig.5 imply that the amount of adsorbed hemoglobin decreases with increasing salt concentration and obeys the following order of increasing depressions : $Cl^- < SO_4^{2-} < PO_4^{3-}$.

The observed decrease in the adsorbed amount may be explained as follows :

(i) Since the experiments were carried out at pH 12.7 which is quite above the isoelectric point of hemoglobin, the protein molecule acquires a negative charge due to the presence of $-COO^-$, O^- or $-S^-$ type of groups. Now since the ACF surfaces are negatively charged, an electrostatic repulsion will be present between the hemoglobin molecules and the ACF surfaces. Here, the introduction of anions enhances the existing repulsive forces which, in turn, decreases the adsorption. Furthermore, since a greater increase in repulsion will be caused by the PO_4^{3-} ions the sequence of increasing order of depression could also be explained.

(ii) It is well known[23] that in protein molecules the cationic groups (such as $-NH^+-$, $-NH_3^+$ and $=NH_2^+$) and anionic groups ($-COO^-$, O^- and S^-) are the potential active sites involved in their adsorption onto surfaces. In the case of addition of anions or cations to the protein solution, these active sites check the added ions and this obviously results in a decrease in their number and consequently the adsorption. This binding property is exhibited to be more or less of the same degree by all proteins but remarkably shown by albumins[24,25].

We have also studied the kinetics of the adsorption process in the presence of added anions and evaluated various kinetic parameters as summarized in Table 2.

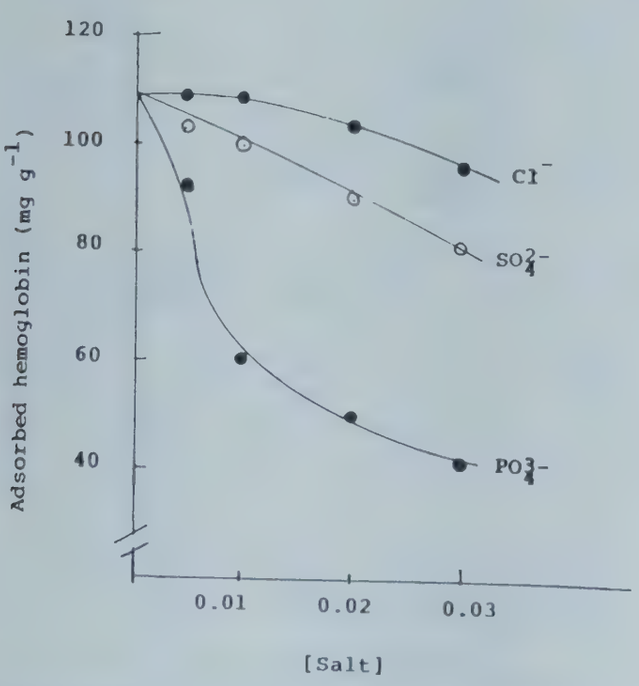

Fig.5 — Effect of addition of salts on the plateau adsorption of hemoglobin at fixed [hemoglobin] $=2.98 \times 10^{-5}$ mol dm^{-3}, [ACF] $=0.2$ g, pH $=12.7$, temperature $=25 \pm 0.2°$ C

Surfactant Effect

The interaction of proteins and surfactants with solid surfaces is of interest both from a practical point of view, in the field of cleaning, and also as a tool to study the binding strength of adsorbed proteins. The surfactants affect the adsorption process in a complex manner; because of their polar ends and hydrophobic chains they can not only influence the existing electrostatic interactions between the protein molecules and surfaces but also get preferentially adsorbed onto surfaces or replace the already adsorbed proteins[26].

In the present study, the effect of surfactants on the adsorption of hemoglobin has been observed by adding a cationic surfactant cetyltrimethylammonium bromide (CTAB) and anionic surfactant (sodium oleate) to the protein-ACF suspension in the concentration range 2.0 to 6.0×10^{-4} mol dm^{-3} which

Table 2 — Various kinetic parameters of the adsorption process in the presence of added anions (0.02 *M*)

Anion	Penetration rate constant	Diffusion constant	Rate constant for adsorption	Rate constant for desorption
	$k_p \times 10^3$ min^{-1}	$D \times 10^8$ $cm^2\ s^{-1}$	$k_1 = 10^4$ $cm^2\ s^{-1}$	$k_2 \times 10^8$ $moldm^{-3}$ s^{-1}
Cl^-	0.70	0.88	12.0	3.63
SO_{42-}	0.82	0.70	9.0	2.72
PO_{43-}	1.21	0.46	6.1	1.84

is well below the CMC's of the surfactants. Figure 6 reveals that the adsorption decreases in both the cases. Also, a greater decrease is seen with the addition of cationic surfactant (CTAB). The results obtained are unusual and can be explained as follows :

(i) The addition of CTAB to the protein solution results in its complexation with the hemoglobin molecules as reported in the case of several other proteins by Wahlgren and Arnebrant[27]. Because of this complexation the diffusion of hemoglobin- surfactant complex molecules is restrained due to their unwieldy dimensions and consequently the adsorption decrease. It has also been observed that the CTAB molecules also get complexed with the already adsorbed protein molecules and cause them to desorb from the surface. This also results in a lower adsorption.

Another reason for the observed depression may be the adsorption of surfactant molecules onto the ACF surfaces. This appears to be justified as the cationic end of the CTAB molecules may preferably occupy the negative sites on the ACF surfaces and thus results in further depression of the adsorbed hemoglobin.

(ii) In the case of addition of an anionic surfactant like sodium oleate the complexation between the surfactant and hemoglobin molecules will also be responsible for the decrease in the adsorbed amount. Also, the anionic polar end of the surfactant enhances the electrostatic repulsion between the hemoglobin molecules and the ACF surfaces and consequently results in a fall in the adsorption.

Solvent Effect

Solvents play a key role in regulating the adsorption kinetics in polar adsorption systems as a change in polarity of the medium directly influences the adsorbate-adsorbent interactions. However, in the case of a hydrophobic adsorbent like ACF the polarity of the medium does not much contribute to the adsorption characteristics. In the present study the effect of solvents on the adsorption of hemoglobin has been investigated by addition of 5 per cent (v/v) aliphatic alcohols to the adsorption system. The results are depicted in Fig.7 which reveals that on addition alcohols the adsorption decreases and the effectiveness of the alcohols increase in the following sequence — t-BuOH < iso-PrOH < EtOH < MeOH. The cause for the observed decrease in adsorption may be explained by the fact that on the ACF surfaces micropores are present which have pore sizes of the order of <20 nm. When the alcohols are present in the ACF-hemoglobin suspension the alco-

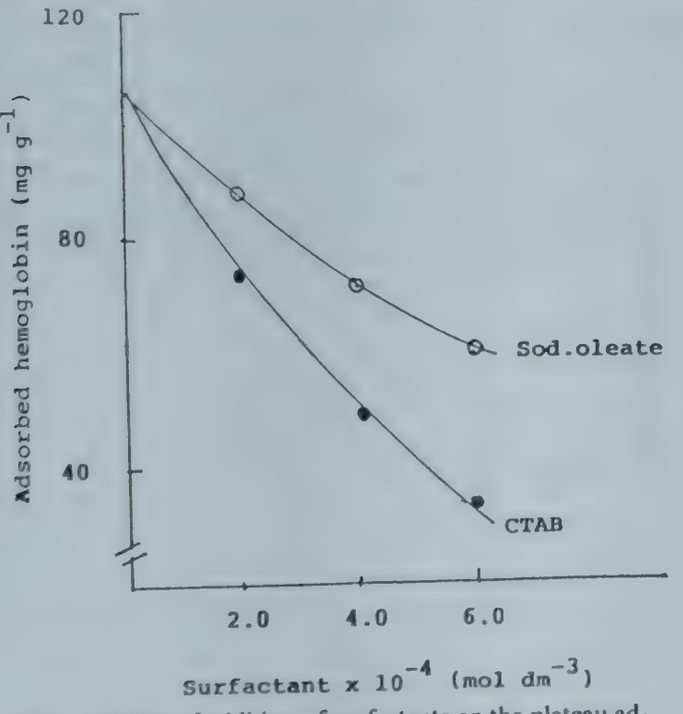

Fig.6 — Effect of addition of surfactants on the plateau adsorption of hemoglobin at fixed [hemoglobin] $=2.98 \times 10^{-5}$ mol dm^{-3}, [ACF] =0.2 g, pH =12.7, temperature =25 ± 0.2°C

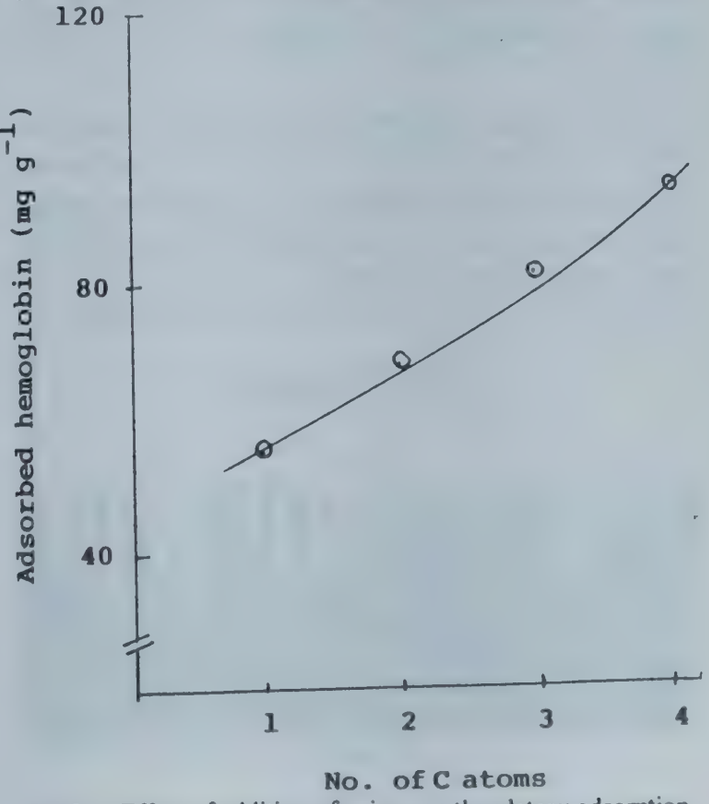

Fig.7 — Effect of addition of anions on the plateau adsorption of hemoglobin at fixed [hemoglobin] $\cong 2.98 \times 10^{-5}$ mol dm^{-3}, [ACF] =0.2 g, pH =12.7, temperature =25 ± 0.2°C

hol molecules diffuse readily to the micropores of the ACF surfaces and occupy the active sites. Thus in comparison to the hemoglobin molecules greater number of alcohol molecules approach at the ACF-solution interface and gets adsorbed. This explains how the adsorption decreases in the presence of alcohols. The preferential adsorption of alcohols is shown in Fig.8. Thus, the relative adsorption of various added aliphatic alcohols depends on their sizes, i.e., a small sized alcohol molecule diffuses more readily from the bulk and gets adsorbed at the interface. In this way, the observed sequence of effectiveness of the added alcohols is also explained.

Temperature Effect

The effect of temperature on the adsorption has been investigated by carrying out adsorption experiments in the range 5 to 45°C. The results obtained are shown in Fig.9 which indicate that the adsorbed amount as well as the rate of adsorption decreases with increasing temperature. The results are attributable to the following facts :

(i) Since the adsorption appears to be of physical nature, the physical forces involved in binding hemoglobin molecules to the surface are weakened at higher temperature and, therefore, the adsorption decreases.

(ii) One cannot rule out the possibility of agglomeration of hemoglobin molecules at lower temperature as postulated by Giles *et al*[28]. Evidently, in this agglomerated state the hemoglobin molecules will be adsorbed to a greater extent.

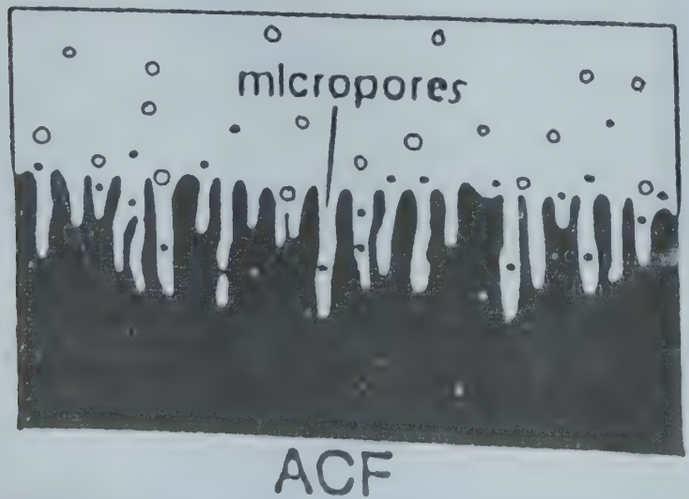

Fig.8 — A model for the preferential adsorption of alcohols at the amicropores of the ACF (•) alcohols, (o) hemoglobin

(iii) When the experimental temperature is high the escaping tendency of the hemoglobin molecules from the solid to the bulk phase increases due to increased solubility of the hemoglobin[29]. This results in a lower adsorption at higher temperature.

Thermodynamic Parameters

We have also calculated the following thermodynamic parameters :

(i) The standard free energy (kcal/mol) was calculated by using Eq.(6)[30].

$$\Delta G^\circ = RT \ln K, \qquad \ldots(6)$$

where K being the equilibrium constant of the adsorption process. The value of ΔG°, as calculated above, has been found to be 6.20 kcal/mol.

(ii) The apparent heat of reaction-enthalpy, ΔH° (kcal/mol) was estimated using Eq.(7).

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \ldots(7)$$

The value of ΔH° has been calculated to be –5.74 kcal/mol.

(iii) The entropy, ΔS° (kcal/deg mol) of the system was calculated using Eq.(8).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad \ldots(8)$$

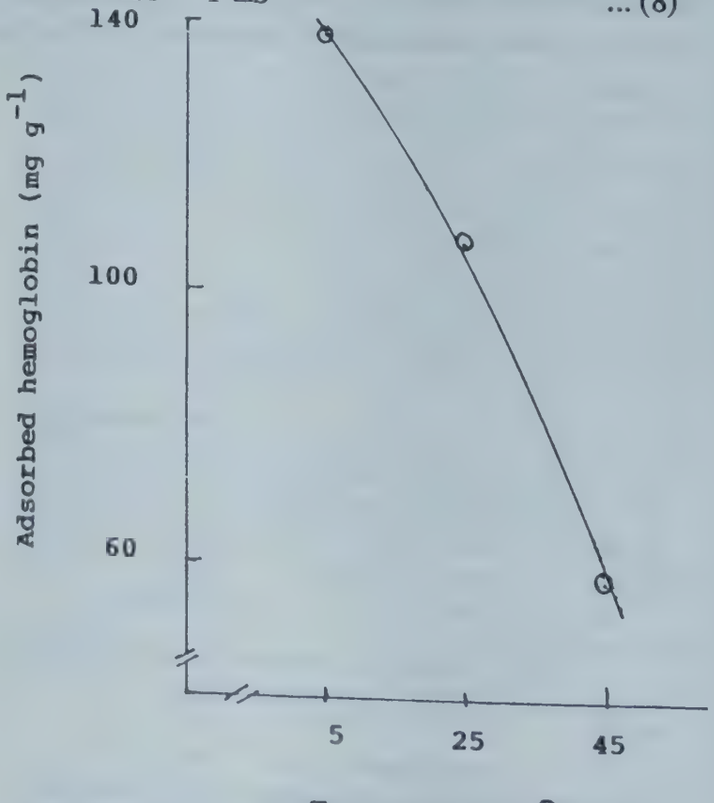

Fig.9 — Variation of adsorbed hemoglobin with temperature at fixed [hemoglobin] $=2.98 \times 10^{-5}$ mol dm^{-3}, [ACF] =0.2 g, pH =12.7

and the value of ΔS° was found to be 1.4 cal/deg mol.

Concluding Remarks

The kinetics of the adsorption of hemoglobin onto the ACF surfaces from the alkaline solution of the protein is studied at room temperature. The adsorption is found to be diffusion controlled and follows the Langmuir model. The adsorption is found to decrease in the presence of additives such as the salts, surfactants, and organic solvents (alcohols). The temperature also has a negative effect on the adsorption and it confirms the physical nature of the adsorption process.

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CONFERENCE REPORT

Thirteenth National Symposium on Catalysis — A Report

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The Thirteenth National Symposium on Catalysis coinciding with the Silver Jubilee of the Catalysis Society of India (CSI) was held at Indian Institute of Petroleum (IIP), Dehradun during April 2-4, 1997. The symposium was organised jointly by the Catalysis Society of India and Indian Institute of Petroleum.

The theme of the Symposium was on almost all aspects of Science and Technology of Catalysis. However, the special emphasis was on the novel applications in applied catalysis related to petroleum refining, petrochemical speciality and fine chemicals and the environment. Other areas of interest to the symposium were natural gas conversion, novel materials, reaction engineering, and structure-activity relationship.

The symposium was attended by more than 400 delegates worldover including almost 100 young research scholars working in the field of catalysts development. Twenty-seven foreign delegates from thirteen countries also participated. One of the significant features of this symposium was participation by a large number of delegates working in private/multinational R&D institution.

The symposium was inaugurated by Prof. M G K Menon, former DGSIR, Secretary DST and Scientific Advisor to PM. In his inaugural address, he remarked that the science of catalysis and its practice in the country will take on newer dimensions in the coming decade as its commercial importance has now been established beyond doubt and the challenges posed and solutions evolved by research would enhance its development. Addressing the participants, he said, although catalysts have been used since ancient times, however, the first use of nickel catalyst was recorded a century ago. He expressed hope that in the near future the catalysis would bring a far greater science based transformation in the world. He also said that the concept of science based industry had gained ground in the country only after Independence and was now widely prevalent. Catalysis, with its possibilities of producing a new range of products, was poised to play a crucial role in the technological development of the country.

Earlier, welcoming the guests, Dr T S R Prasada Rao, Director, IIP who was also the Chairman of the National Organising Committee of the symposium, said the participation of a large number of foreign experts in this Silver Jubilee Symposium of the CSI was a source of inspiration for the scientific community of the country. In his welcome address, he said that India has made a global impact in the field of fertilizer catalysts and their production. He said that the present world without the fruits of catalysis is very difficult to imagine. Catalysis being a critical field of applied science interfaced with technology is vital to the economy. He hoped that the symposium will certainly stimulate and catalyze the advancement of catalytic science and its wider industrial applications. He also hoped that deliberations and interactions will provide an opportunity to realise the immense potential of this evergreen field of science in making this world more safer and comfortable in the 21st century.

Speaking on the occasion, Dr Paul Ratnasamy, Director, National Chemical Laboratory, Pune and Co-chairman, National Organising Committee said that Catalysis Society of India has given a chance to

*For correspondence

academy and industry to come under one platform to have close interaction. He stressed on the need for releasing more funds for catalysis research which he said, "had not reached the point of diminishing return" as was believed by some people. "The major fruits of the research would come to the light in the future", he said.

Dr N M Gupta, President of the Catalysis Society of India, briefed the audience on the history of CSI over the past 25 y since its formation at Banaras Hindu University in 1973. He said that the CSI in coordination with the Council of Scientific and Industrial Research (CSIR) and Department of Science and Technology (DST) played an important role in initiating various international exchange programmes in Catalysis. He also announced the names for the Eminent Scientist Award, S Kameswari Young Scientist Award and Rev Fr L M Yeddanapalli Prize. Later in a glittering ceremony the CSI's Eminent Scientist Award was presented to Dr T S R Prasada Rao, Director, IIP and Dr S Sivasanker of the NCL in recognition of their major and significant contributions to catalysis science and its practice, by Prof. M G K Menon. The S Kameswari Young Scientist Award of the CSI for the year 1996 was presented to Dr R Vetrivel of NCL, Pune, while the Rev Fr. L M Yeddanapalli Prize was given to Dr A Keshavaraja again from NCL, Pune.

Dr G Murali Dhar, Convenor of the symposium, briefly introduced the audience to the theme of the symposium. In his address, he said that the symposium would cover various aspects of catalysis, reaction chemistry, catalytic processes and novel catalytic materials for various applications. "Particular emphasis being given to novel applications in applied catalysis related to petroleum refining, petrochemicals, fine chemicals, as well as the environment", he said. He informed that the symposium received sponsorship and financial support from many industries, leading research organisations and institutions. These included Council of Scientific & Industrial Research, Department of Science & Technology, Oil Industry Development Board, Centre for High Technology, Indian Oil Corporation Ltd, Bharat Petroleum Corporation Ltd, Oil & Natural Gas Corporation Ltd, Gas Authority of India Ltd, UOP Asia, Condea, AG, Germany, Fine Tech Instruments Corporation, Indo-Burma Petroleum Company Ltd, Indian Petrochemical Corporation Ltd, Bongaigaon Refinery & Petrochemical Ltd, Madras Refineries Ltd, Cochin Refineries Ltd, Reliance Industries Ltd, Mangalore Refinery and Petrochemicals Ltd, Essar Oil India Ltd, Oil India Ltd, Hindustan Organic Chemicals Ltd, Gujarat Narmada Valley Fertilizers Co. Ltd, Gujarat State Fertilizers Co. Ltd, Adarsh Chemicals & Fertilizers Ltd, United Catalysts India Ltd, SBI, IIP Branch, Chemito Instruments Pvt Ltd, Department of Atomic Energy and Bruker India Scientific Pvt Ltd.

Later, Mr V K Kapoor, Head, Catalysis Division, IIP, while thanking all the dignitaries concluded the inaugural session with his own perception regarding catalysis science. He also expressed his gratitude to all the participants who came from different parts of the country and world and made this symposium a success. He also drew attention towards the message of appreciation and good wishes received from: (1) Prof. Y K Alagh, MOS, S&T, GOI, (2) Mr V L Kelkar, Secretary, Ministry of Petroleum and Natural Gas, (3) Prof. V S Ramamurthy, Secretary, DST, (4) Dr R A Mashelkar, DGSIR, (5) Mr G V Rama Krishna, Chairman, Disinvestment Commission and (6) Prof. Eric G Derouane, President, Liverhulme Centre for Innovative Catalysis, UK. He regarded these messages as a measure of interest, the scientific community has in the field of catalysis.

Eminent Scientist Award Lecture

Besides the plenary and technical sessions at the symposium, there were two eminent scientist award lectures delivered by the winners of the CSI's Eminent Scientist Awards. Delivering this special lecture Dr T S R Prasada Rao, Director, IIP spoke on the modification of catalytic functions of ZMS-5 with special reference to aromatization. He discussed the role of acid insoluble extra framework aluminium in generating the acid sites of enhanced strengths and its relation to aromatic yields. The role of Ga and Zn in altering the catalytic pathways for aromatization of various hydrocarbons were also discussed.

The second lecture of this series was delivered by Dr S Sivasanker of NCL, Pune. In this lecture, Dr Sivasanker discussed the location of the metal in metallosilicate molecular sieves. Citing an example of vanadium in vanadosilicate molecular sieves he stressed on the need for a careful examination of

these metallosilicates by a combination of many characterization techniques and catalytic activity.

Plenary Lectures

The first plenary lecture was by Prof. W M H Sachlter (Department of Chemistry, Northwestern University, Evanston, USA) who gave an exhaustive account of the catalytic isomerization over metal acid and hybrid sites.

The second lecture was delivered by Prof. Y Iwasawa (Department of Chemistry, University of Tokyo, Hongo, Japan), who in his lecture, reviewed the recent work dealing with designed active structures at oxide surfaces and their spectroscopic characterizations in an atomic or molecular scale.

Prof. M Che (Laboratorie de Reactivite de Surface, CNRS, Universite Pet M Curie, France) in his lecture presented the approach for investigating the molecular aspects of catalyst preparation, when simple molecular precursors interact with conventional oxide supports.

The fourth lecture by Prof. L Guczi (Department of Surface Chemistry, Hungarian Academy of Sciences, Hungary) focused on some problems on environmental catalysis. He discussed the optimization of catalytic processes involving NO_x abatement and total combustion of hydrocarbons.

Delivering the fifth lecture, Dr Jens R Rostup Nielsen (Haldor Topsoe, Denmark) spoke on steam reforming of liquid hydrocarbons.

Prof. P G Menon (Department of Chemical Engineering, Royal Institute of Technology, Sweden) delivered an absorbing talk covering catalytic combustion for pollution abatement and cleaner thermal power generation. He stressed the need for development of novel materials such as substituted barium hexa-aluminate for catalytic applications above 1000°C for sustained operations.

In the seventh lecture, Dr R Prins (Laboratory for Thermal Chemistry, Federal Institute of Technology, Switzerland) pointed out on the effect of P and F in the hydrogenitrogenation of *o*- toluidine and 2-methylcyclohexylamine by kinetic modelling.

Technical Session

The presentation of the invited and contributory papers at the symposium was organised under the following sections: (1) Zeolite Catalysis, (2) Oxide Catalysis, (3) Metal Catalysis, (4) General Catalysis, and (5) Homogeneous Catalysis. The whole session was further divided into 15 subsections:

1	Novel microporous materials,
2	Acid catalysis by solid materials,
3	Industrial Catalysis,
4 and 5	Homogeneous catalysis I and II,
6	Theoretical and photo catalysis,
7	Supported metal catalysis,
8	Environmental catalysis,
9	Selective chemical transformations by zeolites,
10	Zeolites in aromatization reactions,
11	Chemistry of zeolite catalysis,
12	Catalysis by metal oxides,
13	Clays as catalysts and supports,
14	Supports synthesis by non-conventional methods, and
15	Future directions in applied catalysis.

Each of the five sections comprised oral and poster presentations besides some invited lectures.

Section 1 — Zeolites

The first invited lecture by R Vetrivel (NCL, Pune) was on "Integrating the Molecular Modelling Techniques to Conventional Catalysis Research". He outlined the application of this technique in understanding the absorption, diffusion, dissociation and reaction of organic molecules, and organo- metallics inside the micropores of zeolites.

The second lecture was by S J Kulkarni (IICT, Hyderabad) who presented a brief account of the recent trends in the application of zeolites and molecular sieves for the synthesis of speciality and fine chemicals. In his informative talk, he explained that various reactions which can be catalysed by Brönsted, Lewis acids or metal cations can be carried out over zeolites.

In oral presentation session, 30 papers were presented. The paper by Joshi and Mukesh (ICI, Thane) described the effect of water on zeolite catalysed acetal formation. Another paper by Talukdar and Bhattacharyya (Guwahati University, Guwahati) focused on the isomerization and cracking of 1-hexene and *n*-hexane, respectively, over MCM-22 in a continuous flow glass reactor. The paper by Ray *et al.* (IIP, Dehradun) which was presented by N Viswanadhan won the second prize for best oral

presentation described the role of extra lattice aluminium types in activity and deactivation patterns of ZSM-5 in *n*-heptane aromatization reactions.

Thirty-three papers were displayed in the first poster session and quite a few of them created interest amongst the audience. The papers singled out for special mention are the ones presented by Deka and Vetrivel (NCL, Pune) on "Adsorption and Diffusion Characteristics of *p*-Isobutylethyl-Benzene in Large Pore Zeolites As Derived from Molecular-Modelling Methods"; Raghavan and Sivasanker (NCL, Pune) titled, "Vapour Phase Alkylation of Benzene with 1-Heptane over Mordenite"; Karuna *et al.* (NCL, Pune) titled, "*n*-DBA - VPI-5": Synthesis and Characterization.

Section 2 — Oxides

Nineteen oral presentation in this session encompassed authors from all corners of the country, though only a few of them had impact. Among these was the presentation by Vijayalakshmi *et al.* (IPCL, Baroda) which also won the third prize for best oral presentation. The work by Srinivas *et al.* (IIP, Dehradun) titled, "Support Effect Studies on TiO_2-Al_2O_3 Mixed Oxide Hydroprocessing Catalysts" and Maity *et al.* (IIP, Dehradun) titled "Studies on Sepiolite Supported Hydro-treating Catalysts" were well received by the audience.

Out of 27 poster presented in this session, only a few attracted the viewers. The presentation by Mulla *et al.* (NCL, Pune) which also won the second prize for best poster presentation described the oxidative dehydrogenation of ethane to ethylene over Sr- promoted La_2O_3 catalyst supported on low surface area porous catalyst carrier. The paper by Wilson and Viswanathan (IIT, Madras) titled "Catalytic Combustion of Carbon on Supported Oxides" also drew lot of interest in which base metal oxides as alternatives to noble metal based catalysts have been reported to be potential catalysts for oxidation reactions.

Section 3 — Metals

The invited talk at this session was delivered by Dr K R Krishnamurty (IPCL, Baroda) on "Modifications in Supported Metal Catalysts: Effect of Promoters". In this interesting talk, recent development in the area of alkali metal promoters were discussed which control acidity in supported metal catalysts.

The oral presentation in this session included nine papers of which the best paper titled "Relationship between Acidity and Catalytic Activity of Chlorided Al_2O_3 supported Pt-Sn Catalysts" was presented by Bajaj *et al.* (IIP, Dehradun). It described the preparation of a series of chlorided γ-aluminas with varying chlorine on γ-Al_2O_3 impregnated Pt and Sn metal on it.

Of the eleven research papers included in the poster presentation, the paper demanding a special mention for its quality was by Xavier *et al.* (UCIL, Cochin). It described the support effect on Cu-Cr/Al_2O_3 catalysts for CO-oxidation in which it was observed that Cu-Cr based catalyst showed better thermal stability than Cu catalyst. This paper also won the first prize for best poster presentation. Another paper in this session which bagged the third prize in the poster presentation was by Babu *et al.* (IIT, Madras) describing electrocatalytic oxidation of methanol on platinum based catalysts.

Section 4 — Homogeneous

This section received a moderate response and fourteen papers were slated for presentation and most of them were quite interesting. The best paper at the session was from Athilakshmi and Viswanathan (IIT, Madras) who described the homogeneous oxidation of alkyl benzene catalysed by heteropoly compounds. Another paper titled "Catalytic Air-blowing Process for Bitumen-Kinetic Aspects" was presented by P K Jain *et al.* (IIP, Dehradun) who highlighted the results of an extensively carried out experimental study in a batch reactor. The paper by Uma Parmeshwaran *et al.* (ACC, Thane) won the first prize for best oral presentation. It described the NO_x abatement catalyst low SO_2 oxidation activity.

Out of fourteen posters displayed in this session, only a few presented the mechanistic insight into homogeneous catalysis. The presentation by Krishnan and Vancheesan (IIT, Madras) titled "An Improved Heterogenized Manganese Complex with More Active Sites As Oxidation Catalyst" was quite interesting. In an attempt to find cheaper and less expensive catalyst system, Halligudi *et al.* (CSMRI, Bhavnagar) displayed the mechanism for homologation of methanol catalysed by Mn (Salen) Cl_2 complex encapsulated in zeolite Y.

Section 5 — General

This section had three invited lectures, eight oral presentations and five papers for poster presentation.

The lecture delivered by V N M Rao (Du Pont, USA) was most interesting. It focused on the topic "Designer Catalysts and Catalysis". In his talk, he observed that new ideas emerging from basic research coupled with powerful instrumentation, analytical methodology, modelling, and state-of-the-art engineering and reactor concepts are setting the stage for the development of highly specific catalysts and catalytic processes.

The second lecture by Malladi *et al.* (UOP Des Plaines, Illinois, USA) was related to Technology Development through Partnership. In his informative talk, he explained that how UOP has opened up its new technology development process to the wider technology supply market.

The concluding invited lecture of this session, delivered by A R Oroskar (UOP, Des Plaines, Illinois, USA) was by far on the most absorbing theme of the whole session with the focus on catalytic processes for the future. In his lecture, he emphasized that utilising the drivers like lower cost route for existing products, environmental concerns, improved product quality and new technology concepts, it will be easier to face the challenges and to develop catalytic processes for the future refining and petrochemical industry.

Almost all the papers in the oral presentation were interesting. However, the paper by Diblitz *et al.* (CONDEA Chemie GmbH, Germany) titled "Manufacturing of Raw Materials for the Catalyst Industry" deserved special mention. It gave a concept for reducing scale-up factors to a reasonable ratio and helped to shorten the development of new raw materials for catalytic applications.

Out of five research papers included in the poster presentation the paper that demands a special mention for its quality was by Narayana and Deshpande (IICT, Hyderabad). It described the Acid Activation of Montmorillonite and Effect on Structure and Catalytic Properties.

The symposium ended with a valedictory function presided over by Dr P Ravi Kumar, Director, Centre for High Technology. In his valedictory remarks, he expressed the hope that the delegates must be feeling rejuvenated with the new ideas that they are taking back with them sweet memories about the mega event held at IIP.

Overall the symposium was a runway success and the delegates commended the laudable arrangements made by organizers. The proceedings of the symposium reassured that the young chemocrates bubbling with curiosity will bring about a change in research and teaching in catalytic sciences in this country — A change that will also be catalysed by persons such as Dr T S R Prasada Rao — and those who have concern for the society and are willing to accept newer approaches.

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BOOK REVIEWS

Skill Development for International Competitiveness, edited by Martin Godfrey (Edward Elgar Publishing, Cheltenham, UK) 1997, pp 316, Price: £ 59.95 (hb)
[ISBN 1 85898 551 X]

The above book deals with the most important aspect of human resource development, i.e. skill development. In the present context of globalisation, the strategies of human resource management have given a new impetus to the whole issue of competitive advantage. Economic growth and technological developments of NICs have stimulated a thought process to look into the role of human capital, resulting in a shift in the perspective from 'natural resource' as resource base to 'human capital' as resource. Associated with this are some important thought provoking issues like can human capital be considered a resource? Does it mean that it requires a systematic planning and policy to promote , sustain, and nurture it? How can skill development give a firm and a country the necessary competitive advantage? What should be the role of education and training in skill development? Is government intervention necessary or it can be left to the market forces? These are some of the issues addressed in this book in various chapters. There is a continuity and flow in various issues that the book has dealt with. All the ten chapters together present a theoretical perspective supported by certain empirical cases to emphasize the need for concerted effort by government and the firms for skill development as an activity for having competitive advantage.

The book begins with an introduction by Martin Godfrey, followed by Behrmans important article where he has addressed the issue of skill development within the neoclassical growth theory framework. He has discussed various growth models to put forward an argument for policy intervention to develop, nurture, and support skill development . This is followed by Berge and Wood's article where they start with the premise that human capital provides the necessary Competitive advantage but they have brought in the importance of quality of the human resource. They have differentiated the labour force into three categories: (i) With no education (ii) With basic general education, and (iii) Education with professional training. A country's competitive strength, according to them is seen in terms of its ability to switch over from labour intensive to skill intensive manufacturing capability. Especially for the developing countries, transformation to skill based manufacturing is essential to be a part of this global market.

Having emphasized on the importance of skill based human resource then comes the question of how to accomplish this? Godfrey in his article has addressed this issue within the framework of Lewis economic development model. Godfrey has tried to show that it is essential for any economy to reach labour shortage stage before transcending to the skill based competitiveness. The condition of the labour shortage would necessitate manufacturing sector to generate skilled labour to supplement their requirements. A situation is thus created for transformation. This process once initiated has to be sustained. The case of Indonesia is taken to elaborate upon this point. The transitions in most of the NICs are explained in this way. The subsequent article by Chea on Singapore details out the efforts made by Singapore government in bringing about this transformation. In the case of Indonesia, it is still in the process of change whereas, Singapore has brought about the change through government's concerted efforts. This chapter also brings out the importance of government intervention and also spells out its strategy.

Cassen and Mavrotas and Edwards in the consequent chapters have dealt with the issue of training which is essential for sustaining the skilled manpower. The role of state is though essential, it should synchronize with the requirements of the industry. Lucas in his chapter has also reiterated the need for a coordinated approach by the government and the Industry for training the manpower. Important issues like whether training should be left to the market or

government intervention have been dealt by taking specific cases. The importance of manpower quality and its utility is emphasized. Humphrey has also reiterated the importance of flexibility and quality of human skill necessary to bring in change. For adapting to fast changing technological front what is important is a strong , flexible human resource base. In all this what emerges is the necessity of building a skilled manpower base in accordance with the Industry's requirement. Upgradation of human resource has to be a continuous process.

At this juncture, Nichol's econometric analysis of Costa Rica,has reiterated the importance of quality of manpower which, according to her study, determines the variation among different countries in their ability to trade and compete in the international market. Skilled manpower base provides flexibility which would facilitate structural adjustment. Mere creation of skilled manpower or having only supportive policies for skilled manpower would not provide the necessary competitive advantage. Synchronization of the two is very essential. Lall and Wingnaraja have also come out with a supportive evidence for Nichol's hypothesis. By taking the case of Ghana, they have shown how a country finds it difficult to structurally adjust if it does not have the necessary skilled manpower base. This also brings out the weakness in the Ghanaian technological base at the enterprise level. Government policy without adequate Industry's initiation will not be a fruitful effort.

This is an important and timely book which has dealt with most debated issues on skill development. In the present context of globalisation, this book with a theoretical perspective, strongly supported by empirical evidence on role of skill based manpower is very appropriate for the developing countries . It has very meticulously dealt with the strategies necessary for developing skill to be a global partner. This is an important book for the policy-makers, Industry, and researchers in international trade .

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The Russian Enterprise in Transition — Case Studies, edited by Simon Clarke (Edward Elgar Publishing Limited, Glos GL50 2HU, UK), pp 405, Price: £ 49.95
[ISBN 1 85898 341 X (hb)]

Countries which learnt their economic management for industrialization from USSR now have to learn the opposite from Russia. Russian enterprises are undergoing transition —what is popularly known as transition from state control to private control or privatisation. Countries, like India which had adopted a mixed path of building up strong public sector enterprises with strict control imposed on the growth of private sector, have denounced much of this vaunted policy with the onset of liberalization. In Russia the process began in 1991, and in India it started little early though (say, 1984?) but actual process of liberalization started with the announcement of new industrial policy in 1991. The literature on such transition is quite scanty; the reason being that such a challenge has never been faced by economists or other social scientists earlier. In a hurry, to get into the band wagon of transition, there are many unarticulated, and half-articulated actions or programmes formulated and already launched. Many such programmes finally contribute very little for the benefit of the country or the enterprises in transition.

Simon Clarke and his research group have done a commendable job by documenting such transitions in Russian enterprises— one of the greatest event of this century for the social scientists. This documentation not only helps understanding of the actual process of transformation in Russian enterprises, but also helps articulation of the problem at a much higher level for possible generalization and finally contributes to the knowledge in different branches of social sciences.

The volume under review is the fourth in the series titled, "Management and Industry in Russia Series". The volume is on specific cases of transitions of four important Russian enterprises; which include, Plastmass—one of the pioneers of privatisation, Lenkon; —a light engineering unit which was following the transition through co-operation of employees; two military-industrial giants and a passenger transport enterprise.

The case studies and documentation are as much detailed as possible in sociological studies, focusing on qualitative changes in the social organization of production at all levels of the enterprise.

These cases are preceded by a contribution from Simon Clarke (the editor) titled, "The Enterprise in the Era of Transition". Simon Clarke has raised a few fundamental questions and actually transformed the cases to a higher level of theoretical refinement of the problem.

Is Russian system an irrational variant of the capitalist enterprise? Is the inertia of the existing system the major barrier to change? These are two fundamental questions Clarke has dealt with in his essay in the volume. 'Yes' to the above questions, What Clarke has argued, is a mind set of neoclassical orthodoxy for which, according to Clarke, "reality is no more than a barrier to the realizations of the ideal". "With in the neoclassical model, Russian enterprises are treated as like capitalist enterprises where capitalist rationality is impeded by the imposition of political and administrative control". Clarke, on the contrary, begins with the proposition, "we simply do not understand the dynamics of adjustment in the transition from state socialism to a market economy". He warns, "The fate of the enterprise (Russian) is not merely a matter of profit and loss, it is the fate of the people and their communities.....".

Clarke, therefore, tried to locate the fundamental contradiction in Russian enterprises in terms of the system of surplus appropriation; where the chain of competition for resources within and among shops, enterprises and ministries and centralized control of distribution were the principal barrier to the expanded reproduction of the system.

Another important dimension added in the understanding of the problem of transition of Russian enterprises is the role of money in the Russian economy. It is revealed that "Relations between enterprises are mediated primarily by money-of-account, but this does not function as credit money since there is no expectation that debts will be repaid".

Real value of the insights of the studies in the volume would be realised only by, in addition to the students and researchers, those who are directly involved in such transition processes in various other countries which were following, partially or fully, the Soviet path of industrialization and economic development; and now facing the reality of liberalization and globalisation.

The concrete case in hand is India which as mentioned earlier, had adopted a partial Soviet system, and formally denounced the same to embrace a system popularly called "market-driven" economy. There are policies adopted for gradual "privatisation" of many public sector enterprises. And the basic model followed for this purpose reveals all the undesirable features highlighted in the book.

The present reviewer strongly believes that all the four volumes in the series should constitute the must reading list of the planners and policy-makers in the countries concerned about transition of public enterprises.

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SCI-TECH UPDATE

S&T postulated as integral part of future economic, political and social scenarios

According to Joseph F Coates, the well known science futurologist, scientific and technological developments will be part of future economic, political and social scenarios. He has expressed these views in the book on the first quarter of the next century: "2025 — Scenarios of US and Global Society Reshaped by Science and Technology" (Oak Hill Press, Greensboro, NC).

Coates, with colleagues John B. Mahaffle and Andy Hines, has used in this book the base of four main drivers of change in the modern world — information technology, materials technology, genetics, and energy technology. They have described the developments in these fields against social, cultural, political and personal aspects of society and have done so in the form of narrations written as though the authors are living in 2025.

Citing an example from this book, Wil Lepkowski writes in *Chemical & Engineering News* of 14 July, 1997, that the book's transportation scenario is entitled "People and Things on move". The authors visualize passage of the 1990 Clean Air Act as one of the most critical transportation milestones of the current era. While enlisting future milestones, the book moves to 1998 with Motorola's planned deployment of its Iridium Satellite Network, which brings enhanced civilian use of the once highly secret global-positioning navigation system. That system was recently declassified and several luxury car manufacturers have already equipped their vehicles to use it. Another milestone, also for 1998, is the development of electric cars as zero-emission vehicles. By 2000, a vast US Computer infrastructure will make it possible to use Intelligent Vehicle Highway Systems based heavily on global positioning technology. By 2010, Japan and European Union will be competing for markets in novel non-polluting, efficiently managed transportation.

Another milestone mentioned is the development by US of a magnetic levitation rail transportation system running coast to coast. By 2025, a part (40%) of the US working population will use "tele-commuting" — working from homes — thus, sharply reducing automobile volume on the highways.

Besides transportation, the book is full of many other future scenarios — manufacturing, environment sustainability, information technology, resource management, automation, health care, leisure, population trends and worldwide tensions. Coates lists "global warming" as a subject concerning the whole world.

According to Coates, the future economy will depend on only one set of phenomenon — the products, processes and services emerging from, new scientific and technological developments.

Coates is critical the way market system is being used for evaluating scientific developments. According to him, there are areas important to the society in which the market system simply will not respond; and R&D is one of those. These market failures, according to Coates, come in two categories. First, longer term objectives that the private sector simply cannot, will not, or does not appreciate, such as "fusion" or the "Human Genome Project". Under the second category comes the cases where the market failed right in the middle of economy — in the areas of materials and energy, for example. "All sorts of research is going on in things like photovoltaics, but where is the research going on in the technologies for energy conservation?", he adds. "Where is the research really going in geothermal or in ocean thermal gradients? These are the areas where you can't expect the private sector to invest", he qualifies. He has also cited the example of "macro-engineering" in this area.

Applauding Japan's S&T policy, Coates says, "Japan every five years for the last 20 years has run a major science and technology study involving as many as 2000 people. The Germans saw this, adopted it, took virtually the Japanese survey, ran it in Ger-

many, and it has been a very successful document in terms of shaping what the agenda of R&D should be." Coates wants US also to do the same type of study. And why only US, it should be helpful to all those nations who want to make a sound S&T base.

Coates, 68, has been doing future studies for almost 20 years. Born in Brooklyn, N.Y., Coates received his bachelor's degree in chemistry at Brooklyn Polytechnic Institute and master's degree in organic chemistry from Pennsylvania State University. He worked in Atlantic Richfield for eight years at bench and moved to National Science Foundation in the late 1960s and later to Office of Technology Assessment (OTA). He left OTA in 1979 and founded what is now Coates & Jarratt. His wife, Vary, is also a technology assessment personage, as president of her own firm, the Institute for Technology Assessment [*Chem Eng News*, **75** (No. 28) (1997) p 33-35]. ❑

BSA

Satellite transmission speeds up Web browsing

Since dedicated leased lines are costly, most of the surfing on Internet is done by the modems which are quite sluggish as a result of the use of telephone lines.

A clue taken from digital television may enable the surfers to break the monotony of viewing large files and video by means of satellite beaming. Three major consortia - Philips, Hughes Olivetti and Intel are trying to provide this type of service to surfers who can soon download massive files on Internet at a rate of about 1000 times than the fastest modems could think of. For this, the user of course should have a satellite dish and a special card in his PC. In this innovation, the Internet service provider (ISP) beams up the files from a base station to a satellite which will bounce back to the customer. These can be sent out on the spare capacity used for teletext or use the entire 45 Mb stream used in satellite transmission.

The transmission will use the standard followed for digital video broadcasting for digital TV. Using this standard, ISP can label each Web page or file with a digital marker. This matches a marker that the provider allocates to the surfer who made the original request. The signal is encrypted so that the page or file can be seen by an authorised user. The ISP uses the same marker for billing purposes also. The ISP can continually transmit most often consulted Web pages for the convenience of surfers which minimises the time gap of waiting for the user.

Philips company is about to market a circuit board that plugs into a computer and connects to a satellite dish aerial [*New Sci*,**153**(2073)(1997)22]. ❑

DSRM

Magnetic separation of pollutants by microorganisms

Efforts are on at the Southampton University by the scientists to use the magnetic properties of microorganisms to remove heavy metal pollutants from contaminated water.

The technology developed is patented under the name Feedback Chemostat which involves species of bacteria that occur naturally in sewage, de-oxygenated water and sediments. These bacteria produce a magnetic, iron sulphide coating which attracts and holds heavy metal actinides, rare earths and platinum group metals, after feeding them with correct nutrients.

The magnetic properties of the coatings depend on the composition of the iron sulphide. Even a slight change in the ratio of iron and sulphur atoms may make a drastic change in the magnetism. It is also found that different bugs will produce different ratios. The research group is conducting further study to achieve optimum levels of magnetism of microorganisms.

A new technology known as Vortex Magnetic Separation, is developed at the university which uses a small high-speed separator that uses vortices to achieve exceptional selectivity. The new magnetic separation process will separate a wide range of materials from industrial minerals to blood cells, and can be used in conjunction with Feedback Chemostat to separate adsorbent and bugs [*Technol Partnership Init News*, London, No. 12, December 1996]. ❑

DSRM

One-chip surfing hits the net

Toshiba and iReady, a chip designer based in San Jose, California, are close to putting everything needed to browse the Web and receive and send e-mail onto a single microprocessor.

If a telephone, television or personal organiser is going to be connected to the Net today, it needs to contain all the basic components of a computer—a processor, memory, and operating software. This

may add hundreds of dollars to a manufacturer's costs. The Internet Tuner chip being developed by iReady allows the manufacturers to put browsing and mail features in pagers, mobile phones and personal organizers for just "a few additional dollars". The Internet Tuner chip even then requires an input-output system.

The Internet Tuner takes raw data from a modem or other network connection, recognises Net protocols, translates the incoming information into e-mail or Web pages, and then displays them on the devices they are built into.

The first versions of the chip being made will work only with plain text. Future versions of the chip being made by Toshiba will only work with plain text. Future versions will be able to handle still images, fax, Java applets, video and audio. This means lot of savings. TV-based Web browsers might come down in price, and telephones or faxes might avoid light charges by using the Net for long-distance calls.

The first products to use the chip are expected to be available by the year end. Toshiba will manufacture the chip and products based on it, but other manufacturers will either be able to purchase the chip from Toshiba or license their own designs from iReady [*New Sci*, **154** (No. 2087) (1997) p. 22]. ❑

HKK

Rapid GNP growth by Korea during 1985 to 1995

According to the Bank of Korea, Korea's per capita Gross National Product (GNP) growth was the third highest worldwide during 1985-95.

At 7.6 per cent on the annual average, Korea's per capita GNP increase lagged behind only that of Thailand (9.4 per cent) and China (8 per cent) in the 11y period. The Korean Central Bank's computation is based on a World Bank tally.

GNP measures a country's total output of goods and services, including income from its investments overseas.

As of 1995, Luxembourg recorded the world's highest per capita GNP with US $ 41,210, followed by Switzerland with $ 40,630 and Japan with $ 39,640. Korea was thirtieth out of 209 nations listed in the statistics with $ 9,700. In terms of total GNP, Korea was placed eleventh with $ 435.1 billion in 1995, up two notches from the previous year.

The Japanese had the longest life expectancy of an average 80y, compared with Korea's 72. The shortest life span was Rwanda's 39y.

According to the World Bank figures, women's proportion out of the total economically active population was maximum in the US with 46 per cent followed by German's 42 per cent, Japan's 41 per cent, and Korea's 40 per cent. ❑

HKK

Precision measurement of earth's rotation by ring laser gyro.

Cart Zeiss will install ring laser gyro designed for the measurement of the earth's rotation in a subterranean cave on the Banks Peninsula, in New Zealand.

The gyro will have a relative resolution of 1/10 000 000 over protracted periods of time. This level of accuracy is of particular interest for geophysicists who aim to use these fluctuations to obtain a better understanding of the earth's structure. They will be able to draw conclusions on displacements inside the earth, the continental drift and the incidence of earthquakes.

Unlike seismographs which only measure linear seismic shocks, a ring laser gyro indicates the different rotational components of the seismic shocks.

A further subject of scientific investigation will be climatic research. Changes in the earth's rotation are also caused, for example, by displacements in the earth's atmosphere in the form of high and low pressures.

The body of the ring laser gyro is made of a 1.2 m X 1.2 m block of Zerodur glass ceramic material with a thickness of 180 mm and a weight of approximately 600 kg.

One of the features of Zerodur glass ceramic material is its thermal expansion of virtually zero. This benefit was utilized to ensure that the surface encircled by the laser beam, displays such a high degree of stability against thermal distortions that the extremely high measuring accuracy required is guaranteed.

The Zerodur block is provided with four longitudinal bores for the laser beam, each 1 m long.

In a ring laser gyro, deflecting mirrors fitted at each of the four corners produce a closed, square resonator in which a laser beam can travel in both directions.

On rotation of the gyro, a small difference in frequency is produced between the two beams travelling in opposite directions. This frequency is measured and can be used to determine the earth's speed of rotation with extraordinary accuracy.

This, however, requires constancy of the light paths. If conventional materials had been used for the laser body their thermal expansion would have markedly disturbed the measurement. Hence, the body was manufactured from Zerodur, the only material with a zero thermal expansion.

The machining process at Zeiss involved the cutting of the edges on the gyro body for the attachment of the highly reflective deflecting mirrors. This was followed by the optical polishing of the oblique surfaces.

The oblique surfaces must be polished with such high precision that the deflecting mirrors can be directly attached to these surfaces with out the use of such auxiliary methods as gluing. The technique is called optical contacting and requires a precision of A/4 in the optical machining which means that the finished surfaces should display an accuracy of 0.5/μ [*Opt Laser Technol*, 29(2)(1997)]. ❑

DSRM

Results of microgravity research discussed

Insights gained into fluid physics, materials science, combustion science, protein crystallization and other allied research areas are discussed at the National Academy of Science in Washington, D.C. held in February 1997.

The participants presented results from Laboratory experiments conducted in the ultra-low gravity environment of space concerning the two recent space shuttle missions, viz., on the US Microgravity Laboratory-2 (USML-2) and in spring 1996 on the US Microgravity Platform-3 (USMP-3).

Klauss, a research faculty member in aerospace engineering science at the University of Colorado, Boulder discussed the effect of microgravity on brine shrimp, mammalian cells, viruses, protein crystals, plant seedlings, bio-materials, and microorganisms. It is noted that development of shrimp is accelerated significantly but the morphology of space-and earth-hatched shrimp is similar. The space product has commercial potential as models for assessing toxicological effects.

Experiments conducted on bone tissue produced by chick osteoblasts grown in space appears to be less dense than that produced on earth-grown control cells. This research on osteoblasts may give some clues to lead to the development of pharmaceuticals that would counteract the loss of bone mass in astronaut's space shuttle experiments have also provided some findings that could have applications in immunological research and drug development.

Jeffrey D Smith, a research associate at NASA reported that studies on space-grown plants gave first evidence that plants physically adopt to a life in space by changing their sensitivity to gravity.

According to Caster, President of New Century Pharmaceuticals, Huntsville, Ala, successful experiments on crystal growth were the "highest diffracting crystal and the largest crystal to date" of a DuPont Merck HIV protease complexed to a proprietary inhibitor, and "the best structure obtained over three flights" for human anti-thrombin (a protease inhibitor that controls blood coagulation).

Earlier studies on xenon in space environment were carried out regarding its behaviour at its critical point with a view to providing insight into fluids, glasses, magnets, liquid crystals and superconductors.

From the data obtained from USMP-3, scientists could calculate xenon's critical temperature to within 100 μK of xenon's critical temperature [*Chem Eng News*, 75 (9) (1997) 37-38]. ❑

DSRM

New Cryptographic system using quantum physics principles

The biggest drawback in 'cash transactions and other sensitive information transmission over networks is the fear of its being decoded and used fraudulently to the detriment of financial companies, banks etc. Many cryptographic codes have been designed but none of them is so far, a foolproof system. The existing systems have no clue to it whether the transmission of the sensitive information was tampered in between.

British Telecom (BT) has developed a way to send credit card numbers or bank details over a network so that users will know if the data have been intercepted by an eavesdropper.

In the conventional cryptographic systems, information is sent in a coded form along with a Key (a string of zeros and ones) to the receiver. The receiving person cannot find whether the key sent to him has been intercepted en route over the network.

Paul Townsend of BT has demonstrated a new method called quantum cryptography which uses the principle that at a quantum level, the very act of measuring certain properties of a particle changes those properties. In this system, information is sent down an optical cable as a stream of light pulses. The phase of each pulse could be 0, 90, 180 or 270 degrees. The eavesdropper has to conduct two tests to find about the correct combination for representing 1 and 0. In that process of trial, the measurement of phase itself will change the phase of the pulse. The genuine receiver, however, has a facility to get the correct information from the original author who informs which bits are to be discarded as suspect.

The system's significance can be gauged from the possibility of developing a 100 per cent secure as long as the fundamental principles of physics are correct as expressed by Richard Hughes of Los Alamos National Laboratory, who is working on a similar system. This fundamental physics question turned into commercial application may be a reality in about three years [*New Sci*, **153** (2064) (1997) 20]. ❑

DSRM

Spectacles with a telescope

Problems connected with poor vision for common man are so far solved by means of glasses, contact lenses for the personality- conscious sophisticated clientele and some surgery in the eye.

A North Carolina team that included Henry Greene, an Associate professor of Ophthalmology at the University of North Carolina and Robert Beadles of Elam, a local technology company has developed a device that is quite different from the prevalent ones to improve the vision in which a telescope is mounted on a special spectacles frame that focusses automatically.

The new device consists of a telescope and an IR beam mounted on the frame. The focusing system in the device measures the distance to the object being observed at the rate of 40 times a second. Then the beam focuses on the object like a point-and- shoot camera. When the distance changes, a built-in microprocessor moves the object lens by driving a 5g motor. The motor moves the object lens in a matter of quarter of a second that it may be taken as almost instantaneous. The telescope can focus on any object from 30 cm to infinity.

For all practical purposes the telescope can be worn by the user on a special spectacles frame which weighs around 70g. Power for the telescope is supplied by a rechargeable battery that can be carried in a pocket.

According to Greene, their device can help people with any visual disorder that responds to magnification. It is felt that the new spectacles can help people with blind spots as it can make objects large enough for them.

The device currently comes only in monocular version and the price initially is a bit high at $3000. Efforts are going on for the development of a binocular design. [*New Sci*,**153**(2070)(1997)20]. ❑

DSRM

Detection of ozone trapped on two Saturn's moons

Astronomer Keith S. Noll, at the Space Telescope Science Institute of Baltimore and colleagues at three other labs, reported that the Hubble Space Telescope has detected ozone trapped on the water ice surfaces of Saturn's moons Rhea and Dione. Scientists had thought such trapped O_3 existed uniquely on the surface of the icy Jovian satellite Ganymede. However, this new finding, reported by Noll, suggested that O_3-created by the irradiation of O_2 trapped within the ice-might be common among water ice-rich bodies orbiting within planets' radiation belts or magnetospheres [*Nature*, **388** (19997) p. 45]. It has been suggested that searching for its spectral signature might be an important strategy for identifying oxygen-containing atmospheres on extra-solar planets because O_3 can be readily detected [*Chem Engng News*, **75** (27) (1997) p. 37]. ❑

HSDK

Unwanted and wanted sound

The control of environmental noise was discussed in 133rd Meeting of the Acoustical Society of America, held jointly with the Institute of Noise Control Engineering (NOISE-CON 97: National Conference on Noise Control Engineering, Pennsylvania State University, State College, Pennsylvania, USA, 14-20

June 1997). It covered all aspects of acoustics and especially active control of noise and vibration. In active noise control, a controlled source is used to cancel out an unwanted sound or vibration. Two schemes are employed either simple feedback or feed forward. In simple feedback the control signal is tweaked to cancel out the unwanted noise and in feedforward a reference microphone is added to sample the source noise, giving a rough value for the control signal directly, and so avoiding the instabilities of simple feedback. Because of their inherent stability, feedforward controllers are generally preferred over feedback controllers. Effective noise control requires the reduction of noise transmission through panels or partitions. In active structural acoustic control, actuators are attached to a panel to change its radiation characteristics. The actuators is a small rigid panel that is driven in a piston-like motion by a moving-coil transducer similar to that of a loudspeaker.

In contrast to 'unwanted sound', the meeting also discussed the design of loudspeakers with improving the quality of 'wanted' sound. Gabriel Weinreich (University of Michigan) has designed and built a loudspeaker with directional radiation pattern that is a strong function of angle and frequency, like violin's output at frequencies above 850 Hz. Weinreich demonstrated the ability of this loudspeaker to reproduce the sound of a violin and a pipe organ. Sound can be 'wanted' for rather different purposes. By recording an incoming sound wave, reversing its time structure and re-emitting it, it can be focused back to its point of origin. Practical time-reversal mirrors, which consist of large ultrasonic transducer arrays, have applications in medicine, in non-destructive testing of solids and in the sea. The experiments conducted in the Mediterranean Sea in April 1996 and May 1997 demonstrated that an acoustic time-reversal mirror can focus sound back to its origin even in an unhomogeneous ocean. This can be used to learn more about acoustic propagation in the ocean and to study fluctuations in currents, temperature and salinity using sound as a probe.

The use of computers to identify the sounds of musical instruments was also discussed by Judith Brown (Wellesley College and MIT). The most successful schemes for identifying human speakers rely on the formant structure of speech sounds. Identifying the formants of each speaker allows a computer to distinguish speakers through pattern recognition. The same procedure followed by Brown for the oboe and saxophone. It was found that a computer can do very well in identifying oboe sounds, although in the case of saxophones there was little difference [*Nature*, **388** (6643) (1997) p. 628]. ❑

HSDK

GRP piping for pure water

Johnston Pipes Co., in collaboration with Hunting Industrial Coatings, UK, has developed a new type of pipe, GRP H20-E, made from Glass Reinforced Plastics (GRP) and lined with waterline epoxy resin which protects portable water from contamination. The major advantage for the new water pipe is that it is lightweight, is more corrosion-resistant than any other material, it does not require the installation of cathodic protection systems and has a high stiffness resistance to distortion. It also has a smooth internal surface for minimal sliming and maximum velocity, constant outside diameter enabling the pipe to be cut and joined at any point along its length, it can be fitted to individual needs while the push-fit sleeve coupling and captive rubber seal cuts cost and saves time. Its raw materials are essentially inert which contribute to its corrosion- resistance but the composition can also be formulated to meat precise mechanical properties for particular application.

At the time of manufacturing, the raw materials are applied to the inside of the GRP pipe at the spinning mould phase with centrifugal forces keeping them in contact with the surface. The polyester resins are allowed to cure for a short time before the waterline epoxy resin is applied by spray. This application too is carried out while the mould and pipe are spinning, resulting in a smooth mirror-like finish. Within 90 minutes of applying the epoxy lining the pipes can be fully tested by Johnston Pipe's normal quality assurance procedures [*Chem Week*, **42** (51) (1997) p 133]. ❑

HSDK

New design for single-electron devices

Wayne H.Richardson in Stanford's Ginzton Laboratory has proposed a new design for a single-electron device with a key characteristic - the ability to amplify electrical signals in a controllable fashion over a significant range of operating voltages. The

design consists of a gallium arsenide junction between a region where the dominant carriers of electrical current are electrons (n-type) and a region were the dominant carriers are holes, that act as positively charged particles (p-type). The gallium arsenide is doped with different kinds of impurities to produce these two conditions. The material has been so heavily doped that it becomes degenerate. In this condition it has electrical properties similar to those of a metal.

The electrical properties of a material are determined mainly be electrons in the higher energy bands, where they can move freely. In metals, the bands overlap and are only partially filled so that it is easy for electrons to jump into the upper energy bands. Therefore, metals conduct electricity so readily. In insulators, there is large gap between the lower and upper bands very few electrons can jumps, so the lower bands tend to be fully populated while the upper bands are nearly empty.

Therefore, they are poor electrical conductors. Semiconductors are an intermediate case. It takes more energy for electrons to jump up into the upper bands than it does for metals, but the gap is small enough so that material can be switched back and forth between conductive and non-conductive conditions. Its electrical characteristics are highly sensitive to the amount and type of impurities in the material. In a degenerate semiconductor, an impurity that provides extra electrons has been added so that electrons are present in the upper bands, forcing it to much like a metal.

Richardson has shown that when a degenerate p-n junction is cooled to temperatures close to absolute zero, it will act as single-electron diode, a device that allows electrical current to flow in one direction, but not the other. Diodes are key components in electronic circuitry. The simplest type of transistor is basically two diodes hooked together. The design exhibits a key characteristic that should allow this material to function as a field effect transistor. In its most basic mode, a transistor acts as a current or voltage amplifier. When a voltage is applied, a transistor will produce an output current that is a set multiple of the input current. To do this in a stable fashion, the transistor must be capable of producing a controllable saturated current. This provides the basic stability that allows one device to drive another and makes it possible to design integrated circuitry. This key characteristic has been missing from all proposed single-electron transistor designs according to Richardson. He has shown that his junction can produce a tunnelling current of this description, which should make possible the design of robust single-electron devices.

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HSDK

Static-free clean-room vacuum cleaner

TIGERVAC Company in Nottingham has designed and built static-free clean-room vacuum cleaner. The EMI-CWR is designed to be grounded during use and any static electricity that is produced while vacuuming is dissipated through the conductive hose, through the vacuum cleaner and discharged to ground. A ground continuity tester is included with every cleaner to verify ground continuity before use. This elimination of static electricity and static charge build-up products protects sensitive electronic equipment.

The model has a four stage filtration system (upgradable to 5 stages) and used in Class 10 cleanrooms. As the contaminated air enters the vacuum it meets the first stage of filtration - a paper bag with a microliner with one micron efficiency to remove the bulk of the recovered materials. Following this is a double cloth filter (2 stages) and then finally through the ULPA filter. The optional 5th stage is a further ULPA filter used when recovering toxic or nuisance dusts [*Chem Week*, **42** (48) (1997) p 131]. ❑

HSDK

Individual defects in diamond lattices

Jorg Wrachtrup *et al*. of the Institute of Physics at the University of Technology, Chemnitz, have developed a readily available technique for studying individual defects and local strain in diamond lattices at room temperature by combining scanning confocal optical microscopy with magnetic resonance spectroscopy [*Science*, **276** (1997) p. 2012]. They focussed on a luminescent defect called the N-V defect, in which a carbon atom adjacent to a vacant site is replaced by nitrogen, and found that by irradi-

ating the diamond sample with electrons, the number of defect centers produced can be controlled. The fluorescence spectra of the individual luminescent centers were recorded to prove that the fluorescence was due to N-V defects and the fluorescence spectrum doesn't fade over time, even under intense illumination. The ground-state spin alignment of the N-V defects allows electron paramagnetic resonance measurements without an external field.

The magnetic resonance spectra of the fluorescing N-V centers revealed marked changes in the spin parameters among different centers, indicating strain-induced differences in the symmetry of the centers [*Chem Eng News*, **75** (26) (1997) p. 31]. ❑

HSDK

Reducing friction on diamond surface with hydrogen

Using an atomic force microscope in vacuum, physicists at Eindhoven University of Technology in the Netherlands have found that the co-efficient of friction between a silicon cantilever and a diamond surface increases by more than a factor of 100 if the layer of hydrogen typically found on a clean, polished diamond surface is removed. Diamonds and other hard carbon coatings are used to strengthen cutting-tool surfaces and to reduce friction and wear between computer hard disks and read- heads. Surface scientist Miguel Salmeron of Lawrence Berkeley National Laboratory in California explains that removing the hydrogen layer exposes a highly reactive carbon surface capped with dangling bonds. Bringing a body in contact with the reactive carbon causes the two surfaces to bond chemically. These bonds must be broken to allow the surfaces to slide past one another. Capping the diamond with hydrogen, however, quenches the reactivity and forms a low-friction surface [*Chem Eng News*, **75** (33) (1997) p. 43]. ❑

HSDK

Nanolithography via copolymer template

Paul M Chaikin *et al.* at the Princeton University, USA, using copolymer films that self-assemble into well-ordered microdomains as etching masks have imprinted silicon nitride substrates with dense, periodic arrays of nanometer-size holes and dots. Patterned materials such as these, with 100 billion features per sq cm may be used in various applications including fabrication of high-density magnetic recording devices.

Polymer chains in diblock copolymers tend to migrate toward like chains, forming numerous single-polymer domains. In the case of polystyrene-polybutadiene, hexagonally ordered polybutadiene spheres spontaneously form in a polystyrene matrix.

Princeton researchers exploited the chemical differences between the polystyrene and polybutadiene phases by using ozone to selectively remove the polybutadiene spheres from a copolymer film coating a silicon nitride substrate. The remaining film, an array of thick and thin polystyrene regions, is etched with reactive ions. The substrate under the thin polystyrene regions is exposed, so a regular pattern of holes forms in the silicon nitride. In a complementary procedure, the substrate beneath the polybutadiene regions is protected by selectively staining the polybutadiene chains with osmium. Etching leaves an array of raised silicon nitride dots [*Chem Eng News*, **75** (No. 22) (1997) p. 34; *Science*, **276** (1997) p. 1401]. ❑

HKK

Rechargeable lithium batteries

Researchers at the Battery Engineering, Inc., Canton, Massachusetts, USA, have introduced a new line of rechargeable lithium batteries that are long lasting, provide four-times the energy density of NiCd and lead-acid types, available in safe packages.

Battery Engineering's Relion™ Rechargeable Lithium Batteries are available in two types: (1) Lithium Ion Polymer with thin, flexible prismatic packages that can be made into high voltage bipolar stacks and (ii) Lithium Ion Inorganic types offered in AA,C,D and custom sizes. Featuring 500 + charge/discharge cycles and no memory effect, both batteries have per cent self- discharge rates.

Providing 200-and 300 Wh/l energy density, respectively, Relion™ Rechargeable Lithium Ion Polymer and Lithium Ion Inorganic batteries use proprietary nonflammable electrolytes with no lithium metal plating. These 3.7 V nominal batteries are environmental- friendly and can be shipped without restriction.

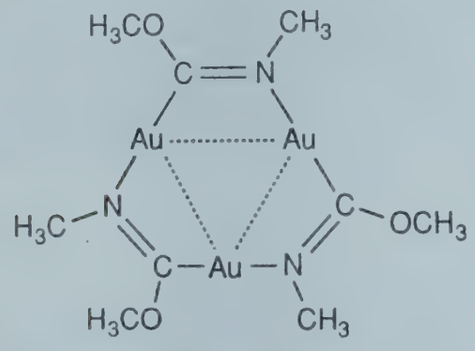
The Relion™ Rechargeable Lithium Batteries are manufactured to customer specifications and priced according to style and quantity. Evaluation samples are available upon request.

For further details, contact:
Battery Engineering Inc.
Sal Piazza, Sales & Marketing Manager
100 Energy Dr Canton, MA 02021, USA. ❑

HKK

A novel trigold complex that shows luminescence after irradiation and washing reported

Gold(I) compounds are well known for their luminescent nature but the researchers at the University of California, Davis, have made a startling discovery. This group, comprising chemistry professor Alan L. Balch, Jess C. Vickery, Marilyn M. Olmstead and Ella Y. Fung, has reported that when the trigold complex shown in structure **1** is irradiated with long-



wavelength UV light (366 nm) and is then washed with a solvent, it emits intense yellow light [*Angew Chem Int Edn Engl*, **36** (1997) 1179].

According to these researchers, the solvent stimulated light emission arises from the solid and not from the individual molecules of the compound in solution. One of the researchers has suggested that UV irradiation causes charge separation, with trapping of the electrons at specific sites, and exposure to liquid triggers charge recombination, with light emission. In the solid, the Au_3 triangles are stacked to form infinite supra-molecular columns, which seem to be important for conducting energy from the bulk to trapping sites near the surface.

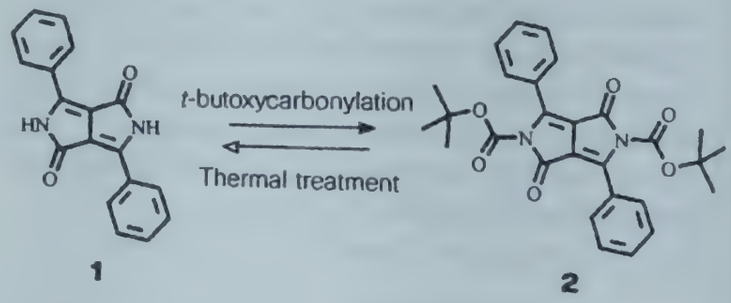
The group now plans to explore the mechanism of light emission and is also studying the potential of this gold cluster as a sensor for liquids and as an energy-storage device [*Chem Eng News*, **75** (No. 26) (1997) 31]. ❑

BSA

Novel homogeneous dispersion of pigments reported

Organic pigments are used as colourants in paints, plastics, printing inks and in electronics industries. However, their insolubility always poses problems and their homogeneous dispersion demands great expenditures of time and energy. But now through a method developed by researchers John S. Zambounis, Z. Hao and A. Iqbal at Ciba Speciality Chemicals Inc, Basel, Switzerland, the dispersion step may be eliminated for organic pigments in paints for particular applications.

The method developed by these researchers, involves converting a pigment into a suitable precursor, a 'latent' pigment, which is readily soluble or homogeneously dispersible in the application medium. Subsequent warming of the latent pigment converts it to the original pigment *in situ*. Zambounis and coworkers have demonstrated the method with a commercial red pigment known as 3,6-diphenyl-1, 4-diketopyrrolo [3,4-c] pyrrole (DPP) (**1**). Its latent pigment was found by replacing the hydrogen in the amino group with tert-butoxycarbonyl groups [$(CH_3)_3$ C-O-C=O] (**2**). The latent pigment dissolved easily in xylene and cyclopentanone at room temperature, whereas DPP is practically insoluble in either solvent. Heating the latent pigment applied on a quartz substrate for two minutes at 180°C regenerated DPP, with release of carbon dioxide and isobutene as elimination by-products.



1 **2**

These researchers claim that their method combines the advantage of dye-like solubility with the solid-state properties of insoluble pigments and could have significant advantage for pigment technology because it simplifies the application process but still allows homogeneous distribution of pigment nanoparticles in a substrate. The technique is applicable to most of the commercial high-performance organic pigments bearing functional groups capable

of reacting with standard protective group reagents. They envisage that their approach might become a powerful tool for probing and even influencing the role of hydrogen bonding in crystal engineering and molecular recognition [*Nature, Lond*, **388** (No. 6638) (1997) 131; *Chem Eng News*, **75** (No. 28) (1997) 36]. ❑

BSA

Diving ability of penguins probed

The ability to dive under water for long periods generally increases with body size, but relative to the best human divers, marine birds and mammals of similar or even smaller size have been found to be outstanding performers. Most trained human divers can reach a depth of a little over 100m in a single-breath dive lasting for 4min but king and emperor penguins (weighing around 12kg and 30kg, respectively) can reach depths of 304m and 534m for as long as 7.5min and 15.8min, respectively. On the basis of their metabolic rates, up to half of the dive durations were believed to exceed the aerobic dive limit (ADL), which is the time of submergence before all the oxygen stored in the body has been used up. But in penguins and many other diving mammals, the short surface intervals between dives are not consistent with the recovery times associated with a switch to anaerobic metabolism.

A team of researchers comprising Y Handrich, J B Charrasin, J Lage and Y Le Maho (Centre National de la Recherche Scientifique, Strasbourg Cedex, France), R M Bevan, P J Butler and A J Woakes (University of Birmingham, UK), and K Pütz (Institut für Meereskunde, Kiel, Germany) has recently revealed the mystery behind this act of gallantry of penguins. According to them, the abdominal temperature of king penguins may fall to as low as 11°C during sustained deep diving. As these temperatures are 10 to 20°C below the stomach temperature, cold ingested food cannot be the only reason of abdominal cooling. It is postulated that the slower metabolism of cooler tissues resulting from physiological adjustments associated with diving *per se*, could at least partly explain why penguins and possibly marine mammals can dive for such long durations. They probably conserve the oxygen and energy that would otherwise have been used to keep this part of the body warm and allow continued aerobic respiration in those parts of the body where it is required most, such as the brain. The cold food that the antarctic animals eat could contribute to this hypothermia, or the aerobic dive limit of penguins might be prolonged by a process of temperature-induced metabolic suppression that is independent of stomach cooling [*Nature, Lond*, **388** (No. 6837) (1997) 64-67]. ❑

BSA

Cell shape determines its fate

Researchers at Children's Hospital and Harvard Medical School, Boston and at the Department of Chemistry, Harvard University have confirmed that the shape of a cell determines whether it will grow or die. Earlier work has indicated that cells that are stretched thrive, whereas round cells do not. Cell growth and survival, however, are also known to depend on the attachment of cells to the extra cellular matrix (ECM) via receptors called integrins.

Donald E Ingber and his team set out to determine whether cell shape or integrin binding governs cell life and death. First, they allowed blood vessel cells to attach to different-sized spherical beads coated with ECM. Fewer cells died on the larger beads, implicating cell stretching as a factor in survival. Then the cells were allowed to attach either to a single path or to several small patches of ECM placed on a nonadhesive surface. If integrins were key to cell survival, they reasoned, the cells would survive and grow equally in either case. It was, however, found that cells that spread on the multiple patches had less tendency to die.

The work may lead to ways for preventing both growth of new blood vessels and spreading of cancer cells in cancer [*Science*, **276** (1997) p. 1345; *Chem Eng News*, **75** (No. 22) (1997) p. 34]. ❑

HKK

Bacterial iron transport: an open-and-shut case

Philip E Klebba and his colleagues at the University of Oklahoma, Norman, USA using electron spin resonance (ESR) have monitored the transport of iron across bacterial cell membranes in real time.

The work supports the hypothesis that "gated" membrane channels in bacteria open and close during iron transport. It also validates the notion that this energy dependent process is triggered by a conformational change in the ligand-binding loops that gate

the entry to the pores through which iron traverses the membrane. Vitamins and other small molecules enter bacteria via small protein channels called porins, whereas iron is transported as a large chelated molecule. The ligand loops are evolved which prevent the entry of large molecules, such as detergents or antibiotics, that are harmful to bacteria.

Klebba *et al*.introduced a nitroxide spin label into an engineered cysteine residue in a ligand loop known as PL5. ESR spectra demonstrated shifts in the mobility of the spin label consistent with opening and closing of the gated membrane channel during iron uptake in live bacteria. In addition, the spectra indicated an accompanying conformational change in PL5.

The discovery may lead to drugs to treat typhoid fever, cholera, gonorrhea, plague, blood poisoning, and other bacterial illnesses by blocking the iron channel of the infecting bacteria [*Science*, **276**(1997)p.1261; *Chem Eng News*, **75** (No.21) (1997) p. 29]. ❑

HKK

Seed-set in *Acacia* flowers in the presence of ant-guards studied

Acacia trees in eastern Africa are protected from insects and other herbivores by ant-guards that patrol the trees' branches and attack any predators they encounter. The ants, in turn, have access to food, shelter, and nest space. It is, thus, probably the best known case of a mutualism between plants and animals. However, as with many defence mutualisms, sometimes the interests of the plant and its defender conflict: for example, when they are in flower the *Acacia* trees require the presence and service of other insects to effect cross-pollination. A question that has been puzzling the biologists was how is pollinator's access achieved in the face of aggressive ant-guards?

Two UK scientists—P.G. Willmer of the University of St. Andrews, Fife, Scotland and G.N. Stone of the University of Oxford—have studied this problem and found that the ants are deterred from young flowers at the crucial stage of dehiscence, allowing bees and other pollinators to visit and transfer pollen. This deterrence appears to be due to a volatile chemical signal from young flowers. The bees and other pollinators are not affected by the repellent and carry off up to 80% of the pollen. Once the flowers have been fertilized, the ants return to their duty, protecting the fertilized ovules and developing seeds.

The repellent is not yet identified but the researchers have proposed that the pollen itself could be its source. The ants' reaction to the repellent is similar to their response to their own alarm pheromones. Therefore, these researchers speculate that, by analogy, the repellent may be a fatty-acid-derived ketone or aldehyde [*Nature, Lond*, **388** (NO. 6638) (1997) p 165-167; *Chem Eng News*, **75** (No. 28) (1997) p. 36]. ❑

BSA

A novel biodegradable polymer for drug delivery synthesized

The polymers that display physio-chemical responses to stimuli are widely regarded as potential drug-delivery systems. Stimuli studied in this direction so far include chemical substances and changes in temperature, pH and electric field. Homopolymers or copolymers of N-isopropylacrlyamide and poly(ethylene oxide)- poly(propylene oxides) - poly(ethylene oxide) (known as poloxamers) are typical examples of thermo-sensitive polymers. However, the use of these polymers in drug-delivery is problematic because they are toxic and non-biodegradable. Most of the biodegradable polymers used for drug-delivery so far have been in the form of injectable microphores or implant systems, which require complicated fabrication processes using organic solvents. These systems suffer from the fact that organic solvents are used in these systems, which can cause denaturation when protein drugs are to be

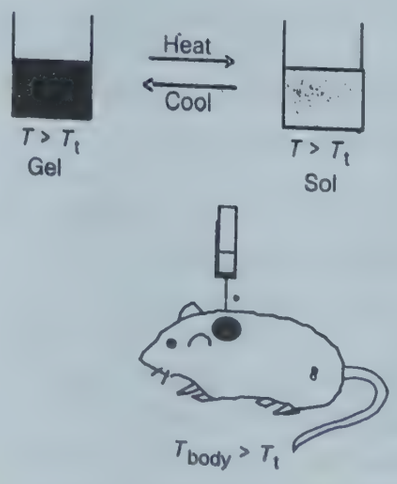


Fig. 1— Injectable drug-delivery system; I_t is the gel-sol transition temperature

encapsulated. Moreover, the solid form requires surgical insertion, which generally results in tissue irritation and damage.

A team of scientists comprising B. Jeong, Y. H. Bae, D. S. Lee and S.W. Kim at the University of Utah, Salt Lake City, USA, has synthesized a novel polymer that possesses a number of unusual properties making it an outstanding candidate for drug-delivery system. Made from the blocks of poly(ethylene oxide) and poly(L-lactic acid), this biodegradable hydrogel is thermo-sensitive. Aqueous solutions of these copolymers exhibit temperature-dependent reversible gel-sol transitions. The hydrogel can be loaded with bio-active molecules in an aqueous phase at an elevated temperature (around 45°C), where they form a sol. The polymer is injectable in this form. Once injected subcutaneously, the sol rapidly cools to body temperature to form a gel that can act as a sustained-release matrix for the drug as it is broken down into non-toxic degradation products [*Nature, Lond*, **388** (No. 6645) (19997) p. 860-863]. ❑

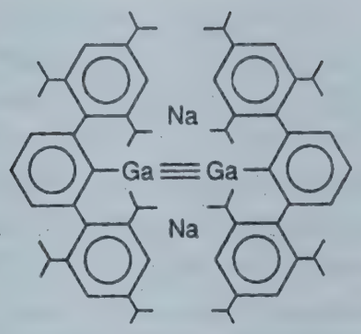
BSA

Synthesis of first triple-bonded gallium compound reported

A team of chemists led by chemistry professor Gregory H. Robinson at the University of Georgia, Athens (USA), has reported the synthesis and characterization of the first compound with a gallium-gallium triple bond.

It may be mentioned here that Robinson and his coworkers had reported two years ago the first cyclogallene — an aromatic ring of three gallium atoms. The cyclogallene was obtained through the reduction of $RGaCl_2$ with sodium metal to yield $Na_2(R\ Ga)_3$, where R was the bulky 2,6-dimesitylphenyl group. Robinson wanted to see what would happen in this reaction if R were an even bulkier ligand than 2,6-dimesitylphenyl group. The team comprising besides Robinson, postdoctoral researchers Jianrui Su and Xiao-Wang Li and graduate student R. Chad Crittendon, decided to try hexa-isopropyl terephenyl ligand, which they refer to "the big ligand".

The team thought that sodium metal reduction of $RGaCl_2$ (where R was the big ligand) might produce a larger all gallium ring, something like $(RGa)_4$ or



Gallyne

$(RGa)_6$. But the compound that they obtained had only two gallium atoms and they were two coordinate, i.e. R-Ga-Ga-R. They also observed that the Ga-Ga bond distance was the shortest ever seen — 2.319Å . The structure also contained two sodium atoms which were on the either side of the Ga-Ga bond, forming a nearly planar Ga_2Na_2 ring. Another intriguing feature of the gallyne structure is that the Ga-Ga-C fragment is not linear, but is bent at about 130°.

Chemistry professor Jerry L. Atwood of the University of Missouri, Columbia, has regarded it as a terrific discovery and adds, "it really opens up main-group chemistry of the heavier elements". On the other hand, Professor Philip P. Power from the University of California, Davis, believes that Robinson's structural data don't support the existence of a Ga-Ga triple bond. In a recent unpublished research, he and his coworkers isolated a tin analog of Robinson's compound — $K_2(RSnSnR)$, where R is a big ligand. They found that Sn-Sn-C angle is about 109° and the Sn-Sn distance is marginally shorter than a single bond: formally it is a double bond, albeit a very weak one.

Robinson, however, is confident about his discovery and feels that his radical proposal will be eventually accepted by all chemists. He adds "some people did not believe their preparation of cyclogallenes too [*Chem Eng News*, **75** (No. 24) (1997) 9-10]. ❑

BSA

Link between leukemia and residential magnetic fields

A new epidemiologic study found no association between acute lymphoblastic leukemia, the most common childhood cancer, and average residential magnetic fields [*N Engl J Med*, **337** (1997) p 1]. It

also found no association between the 'wire code' category of exposure and risk of leukemia. But some previous studies have found associations between this type of leukemia and wire coding but not between leukemia and 60-Hz residential magnetic fields. Marth S. Linet *et al.*, at the National Cancer Institute, compared the living conditions of 638 children with leukemia to those of 620 youngsters without cancer. The residential magnetic fields were measured within 24 months after the diagnosis of leukemia, unlike earlier research in which fields were measured many years after. A tendency for the leukemia risk found to be higher when magnetic field exposure levels were in the higher category 0.300 microtesla or more, but the number of children with such high exposure levels was small so the association may not be significant [*Chem Eng News*, **75** (28) (1997) p. 27]. ❑

HSDK

Health risks of carcinogens in chlorated water

A new study by the National Toxicology Program, headquartered at the National Institute of Environmental Health Sciences (NIEHS), Research Triangle Park, N.C., has focussed on the health risks of potential carcinogens found in chlorinated water and a team of Finnish researchers reported that 3-chloro-4-(dichloromethyl)-5- hydroxy-2 (5H)-furanone, also known as MX, causes cancer in rats [*J Nat Cancer Inst*, **89** (1997) p. 848]. MX is formed when organic matter in water reacts with chlorine during treatment.

Hannu Komulainen *et al.* of the National Public Health Institute in Kuopio, Finland found that drinking water containing MX raised the incidence of thyroid, liver and other tumors in rats. However, limited measurements to date show MX levels in the U.S. and Finnish water supplies are below those used in the Finnish study. Ronald L. Melnick and Gary A. Boormam of NIEHS and Vicki Dellarco of EPA's office of water have noted that the health risk from such levels of MX probably around two cancer cases per million people over a lifetime of drinking chlorinated water [*Chem Eng News*, **75** (25) (1997) p. 28]. ❑

HSDK

A new class of antibiotics

Biochemists in California, USA have discovered new class of antibiotics which may help patients and doctors struggling against antibiotic-resistant infections.

These new antibiotics are based on erythromycin, a common antibiotic. The new compounds are shown to kill bacteria just like erythromycin. The compounds are to be clinically tested before they can be used to fight infections.

The antibiotics were made by alerting the biochemistry of the erythromycin-producing fungus *Streptomyces*.

Generally, *Streptomyces* makes erythromycin by tinkering with a chemical called 6-dEB, which is built up from several small precursor units by an enzyme called DEBS.

DEBS, however, is not particularly fussy. When the normal precursor molecules are not around, the enzyme works with all kinds of precursor units to form strange molecules that are similar but not identical to 6-dEB.

It was decided to cut off the supply of normal precursor by modifying a strain of *Streptomyces* so that it becomes unstable to produce the normal precursor. Then the fungus unusual molecules were fed with extra aromatic rings, carbon chains and hydroxyl groups. As expected, the mutant strain churned out all kinds of strange versions of 6-dEB. These were then fed to another strain of *Streptomyces*, which turned them into the novel antibiotics.

This is for the first time that novel, erythromycin-like molecules have been produced by a method useful to the antibiotic fermentation industry [*Chem Ind*, **No.14** (1997) p. 542; *Science*, **277** (1997) p. 367]. ❑

HKK

The longest bond

Thomas Drews and Konard Seppelt at the Institute of Inorganic and Analytical Chemistry, Free University, Berlin, have found the longest element-element bond—in a green crystalline xenon compound. A xenon to xenon bond could be created in the presence of so-called 'magic acid'.

Xenon was originally labelled as an inert gas, assuming that its full octet of electrons would not react. However, in 60s, xenon was shown to confound the theories by being made to react with fluo-

rine. Numerous fluoroxenon compounds, such as XeF_2, XeF_4, and XeF_6 have since been made and chemists have also attached nitrogen, oxygen and even carbon atoms to xenon.

In the late 70s, a rather mysterious approach, as Seppelt describes it, was used by Lawrence Stein *et al.* at Argonne National Laboratory and Anthony Downs of the University of Oxford to produce the first compound to contain the astounding xenon to xenon bond. Stein and his coworker's compound was made by reducing $XeF^+Sb_2F^{11-}$ using elemental xenon itself, as well as several other reducing agents, the xenon spontaneously reacted at -20°C and the formation of the Xe^{2+} ion was followed using UV and Raman spectroscopy.

Seppelt and Drews repeated the experiments by using the more revealing technique of X-ray crystallography for measuring the length of the alleged xenon-xenon bond. Using a degree of trial and error, it was eventually found that only a xenon-xenon ion could be formed if they used magic acid (hydrogen fluoride with antimony V fluoride) along with a touch of their own alchemyin the form of an interesting coding sequences.

The efforts were successful with the formation of Stein's reported green solution, though it was found that rather than 12 fluorine atoms, the compound obtained had 21. More interestingly, the crystals carried what expected was the Xe^{2+} ion. Researchers measured its length from the crystallographic data and found that it was some measure shorter at 308.7 μm than theoretically predicted. The bond is slightly stronger than expected [*Chem Br*, **33** (7) (1997) p. 17; *Angew Chem Int Ed Engl*, **36** (1997) p. 273]. ❑

HKK

ISI (R) releases two new conference proceedings databases for Current Contents (R) subscribers

The Institute for Scientific Information (R) (ISI) has recently announced the availability of *Current Contents Proceedings* (CC Proceedings) which is a new database option exclusively for current subscribers of *Current Contents* published monthly. The new databases provides an access to recently published literature from the most significant conferences, symposia, colloquia, and workshops in a wide range of disciplines in science and technology (S&T).

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CC is a weekly table-of-contents database which presents the contents pages of current issues of the world's scholarly and technical journal literature, then adds value to that information via the addition of helpful indexes; author abstracts; author keywords and the proprietary KeyWords Plus (R); and reprint author- and publisher addresses. Originally published as a print digest for the life sciences, CC has evolved over the last forty years into a multidisciplinary, multi-platform product that is produced in seven editions; Life Sciences, Clinical Medicine; Agriculture, Biology and Environmental Sciences; Physical, Chemical and Earth Sciences; Engineering, Computing and Technology; Social and Behavioral Sciences; and Arts and Humanities.

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Additions and Corrections

Vol 56, October 1997

Reference	As printed	To be read as
Page 635		
(4th line, right hand column)	accomplished in minimizing the AOX to the level of	accomplished in minimizing the AOX to the level of ~ 0.01 kg/tonne

Vol. 56, November 1997

Reference	As printed	To be read as
Page 659		
(Line 16, left hand column)	Critical[16]	Critical[6]
Page 661 (Reference 10)	Council	Council)

Journal of Scientific & Industrial Research
Vol. 56, 1997, pp 779-806

ANNUAL INDEX

Journal of Scientific & Industrial Research
(Incorporating *Research and Industry*)
Instructions to Contributors

The **Journal of Scientific & Industrial Research** (Incorporating ***Research and Industry***) is published monthly to serve as an information link between the generators and users of technologies. It is addressed primarily to industrial entrepreneurs, technologists, engineers, technocrats and administrators in industry. Therefore, original research articles of practical interest to industry are invited for publication.

Contributions should have an economic bias, and wherever possible, cost estimates should be provided. They should be tersely written, giving only the significant results.

Besides, reviews on various branches of science and technology, science/industrial policy and management are also accepted.

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Scientific Industrial Research

(i)Scientific investigations successful at the pilot-plant and in-plant trials.

(ii)Technology upgradation.

(iii)Development of cheaper and indigenous raw materials as replacement for uneconomical materials.

(iiv)Import substitution.

(v)Technologies for rural development.

(vi)Standardization and quality control.

(vii)Technologies of waste management.

(viii) Industrial R&D highlights.

Technology Management

(i)Success/failure stories in technology management.

(ii)Technology assessment.

(iii)Technology transfer.

(iv)Technology assimilation and adaption in different industries.

(v)Technology funding including venture capital.

(vi)Human Resource Development.

vii)Management.

(viii) Environmental management.

Industrial Development

(i)Policies, programmes and progress.

(ii)Critical profiles of industries—individual and sectoral.

(iii)Technology Forecasting .

(iv)International Collaboration.

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The editors are keen in projecting the technology bottlenecks/problems faced by the industry for their solution by the scientists in various laboratories. They would welcome to be mediators between the industry and the laboratory.

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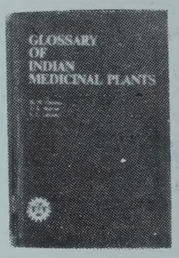

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